

Interactive comment on “Mineralogy and mixing state of North African mineral dust by on-line single-particle mass spectrometry” by Nicholas A. Marsden et al.

Detailed Response to Anonymous Referee #3

Abstract, line 6-7: specify the temporal resolution required

The sentence now states:

but also because of the lack of an efficient method to report the mineralogy and mixing state of single particles with a time resolution comparable to atmospheric processes lasting a few hours or less.

Abstract, line 19-20: please clarify the sentence

Now reads:

In most cases, the difference in composition between particles within a sample was continuous, rather than a collection of particles with discrete mineral phases.

Page 2, line 8: “observations”

Corrected.

Page 2, lines 16-22: this section is confusing; you speak about soil to aerosol partitioning and atmospheric ageing, but this is not very clear

Now reads:

the abundance of mineral phase has a strong grain size dependence, with quartz occurring in the coarse fraction and clay minerals dominating the fine fraction, but the size distribution is modified during emission \cite{Perlwitz2015}, so that ratios of mineral phases in the lofted mineral dust aerosol may not be completely representative of that of the source soil.

Page 2, lines 23-28: also this section is confusing since it mixes considerations on the temporal and spatial resolution of dust mineralogy

Removed the reference to temporal resolution in this paragraph.

Page 3, line 22: the reference by Kok et al. (2017) is not appropriate here since the Kok et al. paper is mostly on the effect of particle size but not mineralogy

Removed reference.

Section 2.1 please add information on the temporal resolution and measurement uncertainties

We have clarified the potential sampling rate in the following sentence:

The instrument is capable of providing size resolved composition measurements for up to 200 particles per second in the size range approx. $0.4\text{--}2.5\ \mu\text{m}$

Added the following paragraph regarding measurement efficiencies.

Laboratory evaluation of the fiber-coupled laser system indicate that the detection efficiency peaks at 0.25 with spherical particles \cite{Marsden2016a}, but the overall efficiency of the instrument also depends on ablation efficiency with respect to particle composition. In a study of nominally pure mineral samples,

\cite{Marsden2017} reported the number of optically detected particles that produced a mass spectra (i.e. ablation efficiency or hit rate) of 0.29 and 0.14 for illite and kaolinite respectively, but was also dependent on the amount of impurities such as Titanium. Furthermore, from the authors own experience, it likely that pure quartz may have an ablation efficiency close to zero and is not considered in our analysis, but is unlikely to be a major component in the fine fraction in any case. The potential maximum overall efficiency of the LAAPTOF measurement of clay mineral ranges from 0.0725 for pure spherical particles particles of illite, to 0.035 for pure spherical particles of kaolinite. The exact efficiency of the instrument is not known in most situations because the size, shape and composition of the particles would have to be known a priori for accurate calibration.

We have also included the following in the conclusions section:

Despite the fact that the technique provides incomplete coverage in terms of particle number, elemental composition, and mineralogy; it was possible to clearly detect regional differences in the mineralogy in single particles of suspended soil and ambient transported dust.

Sect. 2.1.1, 2.2.2, 2.1.3: please reorganize these sections to clarify the methodological aspects, while the aspects mostly linked to discussion of data should be moved to Sect.3 (“Results”)

We have reorganized much of the method section. However, we retain the crystal structure and sub-composition of pure minerals as our method (rather than results) despite the fact there is some discussion of the methodology. This is because we want to make a clear separation of the methodological and scientific aspects of the measurements.

Sect. 2.2: which is the impact of the differences in the sampled size distribution compared to LAAPTOF?

We have added this statement to the start of results section 3.1:

The resulting particle concentration and size distribution is dynamic but is typically on the order of 1000cm^{-3} with a particle size mode at 200nm (See supplement S2), which is below the lower size cut of the LAAPTOF, but not the filter collection. Although the two measurement techniques are not performed on the exact same particle sizes, both measurements represent the fine fraction ($<2.5\ \mu\text{m}$) of the samples, due to the size distribution of the dispersed dust.

Sect. 2.4: the vicinity of the measurement site to the airport runway has an effect on measurements?

The airport was down wind of the sampling. There were only a handful of flights per day, and while some carbonaceous aerosols were detected in association with aircraft activities, they had no impact of the mineral dust in the measurement.

Page 10, line 8: “to analyse”

We have changed this sentence.

Results and Discussion, sections 3 and 4: I invite the authors to consider if some of the aspects in Sections 2.1 should not be moved here and also if the whole presentation of results and the discussion should not be reduced a little bit in length and also made more readable for a non-advanced reader. The text is fact very dense and complicated in some points in my opinion and it could be probably simplified.

Thank you for your advice. We have combined the results and discussion sections in order to reduce the complexity and length of the text. We now have a longer, but lighter conclusion section that is more accessible to the non-advanced reader, whilst maintaining the detail in the results/discussion.

Interactive comment on “Mineralogy and mixing state of North African mineral dust by on-line single-particle mass spectrometry” by Nicholas A. Marsden et al.

Detailed Response to Anonymous Referee #1

Reviewer's comments in black

Authors' response in blue

Changes in the manuscript in green

The analysis presented here could be more fairly put in context of SP-MS analysis focused on mineral dust that has come before, while still highlighting the advance made here regarding distinguishing between mineral phases.

The manuscript now references much of the previous SP-MS analysis that you have brought to our attention. Thank you.

I think the importance of single-particle measurements of mineral phases should be developed more in the introduction to better motivate the work. This is a major challenge that limits our understanding not just of sources and transport of mineral dust, but also of their critical properties. Knowledge of mineralogy (as opposed to just elemental composition) is necessary to understand chemical reactivity, and is crucial to predict the mineral particles' ice nucleation properties.

Because this paper is likely to be of interest to a wide audience, we did not want to put too much emphasis on the ice nucleating properties, which will be further developed in a second manuscript (under preparation by R.Ullrich). However, in order to get a better balance between the dust cycle aspect and the critical properties, we have now refer to laboratory measurements, and ice nucleation more specifically in the abstract. We have also moved the introduction to the role of mineralogy in ice nucleation further up in the introduction section.

The manuscript was often hard to follow, sometimes written more like a lab report with concepts and terms suddenly introduced with no explanation or definition. It was especially difficult to keep track of where the various geographical locations that are mentioned repeatedly actually are. Many of the figures are not designed that well, do not have captions that adequately explain the figure, and could be improved in their clarity. Several sections often start with just one sentence before the subsection starts, an odd way to start a section. Many typos and syntax errors abound, and many references cite ACPD versions of papers instead of the ACP version; the manuscript needs to be carefully proofread and improved. The analysis and results presented here will certainly be of interest to the ACP community. This manuscript should be acceptable for publication in ACP once the authors fully address the questions raised and improve the manuscript's clarity

We have made a considerable effort to make the manuscript easier to follow. The results and discussion sections have been combined, the section headers are clearer and the figure captions contain more details.

Introduction: (Jickells et al., 2005) is an excellent review of the importance of atmospheric mineral dust for the oceans and biogeochem.

This reference has been added.

Pg 3/line 14: It is not really accurate to refer to the “IN fraction”. A fraction of particles can be IN active at a /specific/ temperature. Most mineral phases are IN active at some mixed-phase cloud temperature, even weak ice nucleants such as quartz. Perhaps rephrase to refer to the ice nucleation properties of mineral dust particles (which requires knowledge of the specific mineral phases present).

This sentence has been re-written to: “However, relating IN properties to mineral phase in natural dust particles is much more difficult due to complex mineralogy and mixing state that is difficult to resolve.”

Pg 3/line 16: When discussing ice nucleation it is important to refer to the ice nucleation mode being referred to. While strong acids and SOA added to dust particles can impair deposition freezing, they do not seem to interfere with immersion freezing. Presumably the condensate or reaction product dissolves off in the droplet (Niedermeier et al., 2011; Reitz et al., 2011; Sullivan et al., 2010a, 2010b)

The sentence was incorrect as originally written, but to avoid a detailed review of ice nucleation, the text has been re-written to refer to ice forming mechanism generally: “To complicate things further, cloud chamber studies of silicate mineral dust coated with secondary sulphate and organics have demonstrated that this mixing can alter hygroscopicity and change the ice nucleation efficiency of a particle but is dependent on the ice forming mechanism \citep{Mohler2008,Sullivan2010,Sullivan2010a,Niedermeier2011,Reitz2011}.”

3/22-29: This paragraph rather discounts the many important observations that have been made regarding individual mineral dust composition, aging, and reactivity achieved through offline electron/x-ray microscopy, for example: (Hwang and Ro, 2006; Jeong and Chun, 2006; Krueger et al., 2003, 2004; Ro et al., 2005; Sobanska et al., 2012; Tobo et al., 2009; Zhang et al., 2003).

The authors agree that it this paragraph lacks appropriate summary of previous work. We have altered the text to; “The application of these techniques can differentiate silicate and calcium rich particles and show evidence of heterogeneous reactions in the atmosphere {Ro2005,Jeong2006,Sobanska2012}. However, further differentiation of silicate mineral phase is hampered by the difficulty in leveraging the full quantitative capability of SEM due to particle morphology effects. Consequently, silicate particles are reported in compositional groups, such as the frequently used scheme described by Kandler{2009}, which describes the dominant elemental features but not actual mineral phase.”

Hwang and Ro, 2006; Krueger et al., 2004; Sobanska et al., 2012 are specific to the heterogeneous reaction of calcium containing particles with atmospheric gasses, consequently we have included them in the section 3.2.1 which reports calcium rich particles and reaction products.

4/4: “SPMS...but not differentiate mineralogy.” This is an entirely inaccurate statement. Indeed later in the paper prior use of SP-MS to differentiate mineralogy is presented. But even there much of the closely relevant prior studies using SPMS to analyze dust mineralogy is not discussed or cited. The first detailed look at how dust mineralogy influences the chemistry of atmospheric dust, as well as particle size and mixing state analysis, was presented by (Sullivan et al., 2007a) in ACP. That analysis found that Ca-rich particles accumulated more nitrate and chloride, while Fe/Al-rich particles took up more sulfate, for example. The Sullivan et al. paper cited here focuses on chlorine chemistry in mineral dust (Sullivan et al., 2007b), which is certainly relevant, but the analysis presented in the ACP paper came first and is more closely relevant to the analysis presented here. There is another paper that focuses on organic acids in mineral dust particles using SP-MS (Sullivan and Prather, 2007). I mention this series of papers that use the ATOFMS as I believe they were the first to really analyze in detail the mixing state and mineralogy of individual dust particles using SP-MS.

What was meant to be conveyed is the actual mineral phase in dust particles is not differentiated. The introduction has been modified to convey the analytical challenge associated with identifying mineral phase. This statement has been clarified to better express this:

“Despite these limitations, SPMS can characterise a particle population by classifying particle types and measuring temporal trends in particle number concentrations using cluster analysis \citep{Hinze2006, Rebotier2007, Gross2010}. Although the reported number concentration are also not fully quantitative \citep{Murphy2007}, a relative trend in certain particle types can be achieved. This techniques have been used to discriminate mineral dust particles from other refractory aerosol types such as sea salt \citep{Sullivan2007c, Dall'Osto2010, Fitzgerald2015, Schmidt2016}, but cannot differentiate the actual mineral phase of silicates within dust particles. More recently, a machine learning technique has shown promise with the classification of mineral dusts of similar composition \citep{Christopoulos2018}, but this techniques also requires suitable mineral dust proxies for training data.

The mixing state of dust particle is discussed in detail in section 2.1.3.

Sect. 2.1: More details regarding the particle detection system should be provided. Is this a custom non-standard setup for the LAAPTOF? Nowhere is the typical particle detected fraction (as a function of particle size) presented. This is critical information as the sub-population of total ambient particles actually detected by the instrument can significantly bias the measurements and analysis. The particle detection rate also governs the ability to observe changes in particle composition and sources over short timescales, something that is focused on here.

More details of the typical particle detected fraction are now given the methods section 2.1.

Laboratory evaluation of the fiber-coupled laser system indicate that the detection efficiency peaks at 0.25 with spherical particles \cite{Marsden2016a}, but the overall efficiency of the instrument also depends on ablation efficiency with respect to particle composition. In a study of nominally pure mineral samples, \cite{Marsden2017} reported the number of optically detected particles that produced a mass spectra (i.e. ablation efficiency or hit rate) of 0.29 and 0.14 for illite and kaolinite respectively, but was also dependent on the amount of impurities such as Titanium. Furthermore, from the authors own experience, it likely that pure quartz may have an ablation efficiency close to zero and is not considered in our analysis, but is unlikely to be a major component in the fine fraction in

any case. The potential maximum overall efficiency of the LAAPTOF measurement of clay mineral ranges from 0.0725 for pure spherical particles of illite, to 0.035 for pure spherical particles of kaolinite. The exact efficiency of the instrument is not known in most situations because the size, shape and composition of the particles would have to be known a priori for accurate calibration.

The relevant parameter for LDI is the laser energy power density (W/cm²). What is the laser diameter when it intersects the particle, so this quantity can be reported?

Unfortunately, the exact value if this parameter is not known to the authors. It requires technical information that has not been released by the OEM.

5/5: Just referring the reader to another paper for relevant information is not satisfactory. Please provide a clear summary here regarding the relevant performance characteristics of this LAAPTOF configuration that influences what fraction of particles are actually detected, put in the context of the aerosol populations analyzed here and their associated properties that govern particle sample and detection.

We have added a paragraph that summarises performance characteristics previously reported with this instrument with mineral dust:

“Laboratory evaluation of the fiber-coupled laser system indicate that the detection efficiency peaks at 0.25 with spherical particles {Marsden2016a}, but the overall efficiency of the instrument also depends on ablation efficiency with respect to particle composition. In a study of nominally pure mineral samples, {Marsden2017} reported the number of optically detected particles that produced a mass spectra (i.e. hit rate or ablation efficiency) of 0.29 and 0.14 for illite and kaolinite respectively, but was also dependent on the amount of impurities such as Titanium. Furthermore, from the authors own experience, it likely that pure quartz may have an ablation efficiency close to zero, so that the potential range of overall efficiency ranges from 0.0725 for spherical particles of illite, to almost zero for pure quartz particles. The exact efficiency of the instrument is not known in most situations because the size, shape and composition of the particles would have to be known a priori.”

A discussion of the impact of these efficiencies on the current measurement are discussed in....

5/6: The LAAPTOF is quite similar in design to prior SP-MS instruments. I do not see why the authors think they can only refer to the few prior LAAPTOF papers that have demonstrated quantitative particle analysis. There is a large body of SP-MS work demonstrating the semi-quantitative capabilities, and even truly quantitative analysis if it is done carefully with calibration (Bhave et al., 2002; Fergenson et al., 2001; Gross et al., 2000). The use of SP-MS to determine heterogeneous kinetics is perhaps the best example of quantitative analysis (Saul et al., 2006; Sullivan et al., 2009).

This section is specifically about the LAAPTOF. We have now formed a better overview of the quantitative capabilities in the introduction.

6/1: It would be useful to expand on this weathering of minerals and how that re-

lates to this analysis. Later in the paper feldspars are discussed as indicating less aged/weathered mineral particles, and I think that idea comes from the information presented here, but the connection is not clear. Feldspars can also be converted to the amorphous clays by acid attack, right? (Wex et al., 2014)

This was referring to the consequence of weathering within the soil on mineral composition and is therefore more relevant to the discussion of the results of the soil dust analysis.

6/15: It is not clear if this analysis works for all silicates such as quartz, which is a very

This has now been included in section 2.1 (see above).

6/23: The poor separation of K⁺ and Ca⁺ is an important limitation in this analysis. Please explain the causes of this. Is it specific to the LAAPTOF's configuration? While space charge effects that degrade ion resolution are common in LDI-MS of ion-rich mineral particles, usually K and C can be resolved. The low ionization energy of K can also produce an overly broad ion peak that extends past m/z 39.5 and into Ca at m/z 40. Is this the issue here? Is the LAAPTOF's MS too poor in resolution to resolve K and Ca?

The poor resolution results from both energy focussing and low ionisation energy, but it is not known if this typical of this instrument design. The sentence has been rephrased to:

"In addition, Ca⁺ is not considered because it cannot be reliably resolved from potassium signal at m/z 39 due to peak broadening,"

6/31: The analysis discussed here is of a semi-quantitative (relative) nature, so I don't see why the authors refer to it as "non quantitative". That has a quite different meaning.

The data in figure 3 shows that the elemental composition is not even relative (feldspar appears less K rich than illite). We have clarified the paragraph to be more explicit about what is non-quantitative and what is semi-quantitative (see also comments on non-quantitative below):

Although the elemental sub-composition measurement is clearly non-quantitative with respect to bulk XRF analysis, the measurement is semi-quantitative (relative) with respect to samples of minerals with the same crystal structure. For example, a clear separation between K and Na rich feldspar is apparent in Fig \ref{tern_cal}, which is relative to their actual elemental ratios. This is not true if comparing the clay mineral illite with the framework silicate K-feldspar, which would not be easily distinguishable from each other if plotted in the same space, despite the clear differences in elemental composition. It is therefore necessary to apply crystal structure analysis to achieve semi-quantitative composition and distinguish clay minerals from feldspar when analysing natural soils with SPMS.

Sect. 2.1.2: At the end there really needs to be a summary of what mineral phases can be included in this type of analysis, and which can be distinguished. I was pretty confused as to what mineral phases (such as quartz, or carbonates) are and are not included in the analysis performed here. A good discussion of how reliably the various mineral phases (that can be analyzed) can be discriminated from each other is also

needed. Please be as quantitative there as possible

This section has been re-organised to make it clearer what mineral phases are included. The first paragraph now reads:

“Sub-compositional analysis is used to produce relative composition measurements that can be compared to fingerprints generated from nominally pure mineral samples. Here, the mineralogical composition of dust is considered with the ternary system $\text{Al}^{\text{+}}+\text{Si}^{\text{+}}, \text{K}^{\text{+}}, \text{Na}^{\text{+}}$, cations readily observed in the SPMS of mineral dust (m/z 27, 28, 39, 23 respectively), using the assumption that the fine fraction ($<2.5\ \mu\text{m}$) is primarily composed of aluminosilicate clays and feldspars, which is a reasonable assumption for dust derived from a continental land mass. Quartz and carbonate minerals are not considered with sub-compositional analysis due to the inability to efficiently ablate pure quartz and the apparent lack of a clear carbonate signal respectively. In ambient dust, calcium rich particles are considered separately to aluminosilicate particles.”

We have also clarified the approach in this paragraph:

Although the elemental sub-composition measurement is clearly non-quantitative with respect to bulk XRF analysis, the measurement is semi-quantitative (relative) with respect to samples of minerals with the same crystal structure. For example, a clear separation between K and Na rich feldspar is apparent in Fig [\ref{tern_cal}](#), which is relative to their actual elemental ratios. This is not true if comparing the clay mineral illite with the framework silicate K-feldspar, which would not be easily distinguishable from each other if plotted in the same space, despite the clear differences in elemental composition. It is therefore necessary to apply crystal structure analysis to achieve semi-quantitative composition and distinguish clay minerals from feldspar when analysing natural soils with SPMS.

A discussion of the reliability of the discrimination of mineral phases has been included in the discussion.

7/7: Reactions with ozone will just convert O₃ to O₂ on dust, and not add any material.

The reference to ozone in this sentence has been removed:

“Internal mixing of non-mineral species can occur during soil formation or during transport in the atmosphere where heterogeneous reactions take place on the surface of the particle {Usher2003}.”

7/10: Usually see other more specific ion markers for organics in dust using SP-MS. m/z +43 is common for oxidized organics, and negative ions often have fragments from organic acids (Silva and Prather, 2000; Sullivan and Prather, 2007). Please discuss why only very small organic fragments are observed here. The LDI laser pulse energy of 3-5 mJ is rather high and perhaps caused extensive fragmentation. Also, while organics can “char” to EC ions, C₂⁺ could also come from black carbon that was mixed with the particle. I would be wary of using C₂⁺ to identify organic carbon, it is a generic carbonaceous (OC + BC) marker.

A sentence that refers to extensive fragmentation has been added to the paragraph:

“Only small organic fragments are observed due to the extensive fragmentation of organic molecules.”

We do not actually use the C2 marker to identify organics, we are just pointing out which ion combinations appear in the spectra after the addition of organic material.

7/19: More unique biological ion markers are often observed, such as phosphates, as well as the rather ubiquitous (Murphy et al., 2006) CN⁻ and CNO⁻ ions, if you look at the spectra presented from ATOFMS analysis for example (Creamean et al., 2013; Pratt et al., 2009; Sultana et al., 2017).

Phosphate markers are not unique to biological material as they can be derived from inorganic minerals such as apatite. The following line has been added to the text to clarify: "Phosphate marker PO_3^- is not considered because it could be derived from the calcium phosphate mineral apatite as well as biological material."

7/23: The use of chloride in the analysis is confusing and needs more discussion. Chloride is not only a part of primary mineral components but can also accumulate in dust via transport and uptake of HCl(g) etc. Please better explain the purpose of using Cl⁻ in the analysis, and how that would be affected by secondary sources of Cl in the dust particles.

The sentence has been re-written to:

"The Cl⁻ elemental ion is included despite it also having mixed provenance such as primary chlorides or secondary uptake of HCl, because it is preferentially ionised due to very high electron affinity and therefore is included as a reference that would otherwise perturb the measurement. It is also an indication of the purity of silicate particles as pure fresh silicate should not contain Chlorine."

8/14: Rationing the signals to Si seems to follow the work of Sullivan et al. that normalized to Al. The use of Si is likely more appropriate, especially in this work's focus on silicate minerals. There is also other work that introduced ternary analysis to understand mineral dust composition and aging (Krueger et al., 2003, 2004; Laskin et al., 2005; Yuan et al., 2004).

In this particular case, the text is referring to quaternary analysis with the SEM technique.

Sect. 2.3: Odd to just have one sentence here. It also inaccurately implies that distinguishing between different minerals using SP-MS has never been done before.

This sentence has been removed.

9/14: what are these, and how do they relate to mineral composition? "fluvisols (50%), associated with yermosols (20%), regosols (20%) and solonchaks (10%)."

To avoid a lengthy explanation, the reference to soil types has been removed.

9/15: It took me awhile to realize that these are the locations that each sample was taken from. Would probably be better in a Table.

This has been put into a table.

11/3: greater sensitivity to alkali metals is due to low ionization energy? Please explain. There is too much expected expert knowledge that non SP-MS users will not necessarily know.

This sentence now refers to ionisation energy:

“...a much greater sensitivity to alkali metals in the SPMS measurement than in the established filter technique due to low ionisation energy.”

11/7: where were these soil samples from? Also North Africa?

Yes North Africa, this has been clarified in the text.

11/12: felsic means feldspars?

Feldspar like in composition.

11/19: This is a good example of where a brief reminder of what this “Anti-Atlas” location is would be useful.

Changed to: “Anti-Atlas mountain range.”

12/13: This is why a proper discussion of the LAAPTOF’s detection efficiency versus particle size (for dust particles) is needed. This suggests that the instrument is only detecting 1% of total silicate particles. How much of this is just due to particle size transmission issues, versus the instrument’s actual particle hit percentage?

The detection efficiency of the system is now discussed in greater detail in section 2.1.

12/23: Uptake of HCl by dust observed using SP-MS was a focus of (Sullivan et al., 2007b), which you cite yet oddly do not discuss when very relevant here.

13/2: Tenerife?

“the island of Tenerife in the North Atlantic”

13/31: What metric is “> 0.2”? Ion peak area? How do you decide if a particle has a “significant fraction (> 0.2)”?

The mixing state sub-composition is defined by the ternary system Chlorine - Org-bio - Nitrate as defined in the paragraph above. Org-Bio > 0.2 simply refers to the number of particles where the org-bio fraction in this sub composition is greater than 0.2 (or 20%). The sentence has been re-worded to:

“The number of particles whose mixing state sub-composition contained more than 20% organic-biological material (Org-Bio > 0.2) varies with the dust concentration”

14/11: This dust mobilization refers to the emissions of dust or its transport?
Confusing.

Changed to: “dust emission”

14/23: Can also have nitrate from coagulation with ammonium nitrate, uptake of N₂O₅, etc. (Korhonen et al., 2003; Sullivan et al., 2007a; Zhang et al., 2000). Can't conclude it is all from HNO₃.

Changed to: "The mixing of nitrate with silicate during and after D1 indicates contact with polluted air and is consistent with transport from the North"

14/25: By biogenic source are you referring to sulfate derived from DMS? Explain.

Changed to: "An increase in the fraction of sulphate containing sea-spray aerosol in D2 on the other hand (Supplement S3.5) may be associated with organosulfur containing compounds from biogenic sources in the coastal upwelling region off the coast of Mauritania."

15/11: Some key references to whole rock geochemical analysis would be nice.

Added a reference to ternary analysis in the context of whole rock geochemical analysis. (Pawlowsky-Glahn, 2006)

15/13: Important paper on ternary analysis: (Yuan et al., 2004)

Thank you, this important reference is now included.

15/14: Matrix effects in LDI are mentioned repeatedly but never explained or discussed. Non-experts will be unfamiliar with this important effect.

"The matrix effects arise from the incomplete desorption and ionisation process and the competitive ionisation of atoms and molecular fragments, so that co-variance of analyte signals is relative to ionisation energy and electron affinity of the surrounding matrix \citep{Reinard2008}. In circumstances where the composition of the matrix is known a priori, careful calibration with a suitable proxy can produce quantitative or semi-quantitative measurements of an analyte within a single particle \citep{Gross2000,Bhave2002}. However, if the particle matrix is complex, such as in soils and transported dust, a this type of calibration cannot be made due to the lack of a suitable proxy."

15/28: Is the reader supposed to know where Praia Cabo Verde is? If so I have forgotten so a reminder would be useful

Praia, Cabo Verde is described as the location of our measurements in section 2.4

Page 15: Fractionation of mineralogy versus particle size during transport is never discussed (Arimoto et al., 2004; Gong et al., 2003; Mori et al., 2003). Nor is the size distribution of the different mineral dust types presented, which is a real oversight.

The properties of the dispersed dust is now discussed in the Results and Discussion (Section 3.1), with example given in the supplement.

The fractionation of mineralogy vs particle size is included in the introduction where we make a distinction between the fine and coarse fractions. We now state at the start of the methods section the assumption that

“the fine fraction ($<2.5\ \mu\text{m}$) continental sediment is primarily composed of aluminosilicate clays and feldspars”

15/34: Quantitative information regarding by how much the mineral composition can change over just one hour would be very useful here. How significant a change can occur?

In most of our ambient measurements, relatively large numbers of illite rich particle matrix (ISCM Ratio > 5) suggests a dust source on the NW margins of the Sahara during the summer. However, a rapid change (< 1 hour) towards a felsic/amorphous particle matrix (ISCM Ratio < 1) was observed when back-trajectories suggest direct emission into the marine boundary layer from the West African coast.

16/20: What are these accompanying aircraft sorties? Another example of new ideas that are just sort of thrown out there without proper introduction or explanation.

Changed to:

but it is interesting to note that Price 2018 did not see significant variation in ice nucleating particle (INP) concentration in aircraft based studies of the Saharan air layer during ICE-D, despite geographically widespread sources of that dust.

16/22: As mentioned above, there are more and more specific biological ion markers to use than just CN- and CNO-. Also please summarize the analysis method developed by Zawadowicz, so it can be better understood why it might not be transferrable from the PALMS to LAAPTOF. If both use the same LDI laser wavelength it is likely transferrable.

As discussed earlier, the phosphate ions are not specific to biological material. We did not have the resource to fully test the method of Zawadowicz.

Conclusions: Mentioning the timescale and magnitude under which changes in mineralogy occur would be good information to include here. That seems to be one of the major findings from the ambient measurements.

Due to the re-organisation of the discussion into the methods section, the conclusion is now longer. It now includes this paragraph:

In most of our ambient measurements, relatively large numbers of illite rich particle matrix (ISCM Ratio > 5) suggests a dust source on the NW margins of the Sahara during the summer. However, a rapid change (< 1 hour) towards a felsic/amorphous particle matrix (ISCM Ratio < 1) was observed when back-trajectories suggest direct emission into the marine boundary layer from the West African coast. This episode lasted only a few hours and challenges previous findings from off-line measurements that the source and composition of transported dust only changes on a seasonal basis.

17/9: Really semi-quantitative, not non quantitative. Almost all the analysis presented here is quantitative-based, not just qualitative.

In the extended conclusion section, we have paid greater attention to the quantitation issue in this new paragraph:

These measurements were made under the reasonable assumption that single particles in the fine fraction were composed of either clay minerals or feldspars/amorphous matrix, a distinction that can be realised by the novel crystal analysis technique. Although the SPMS technique is shown to be generally non-quantitative with respect to the elemental sub-composition of pure mineral phases such as illite and K-feldspar, a semi-quantitative (relative) measurement of elemental composition can be achieved after particles are separated into mineral groups based on crystal structure. Further differentiation of mineral phase can then be made by comparison to pure mineral fingerprints from within the mineral group. This indicates the importance of particle structure in addition to particle composition in the matrix effect in SPMS.

17/14: Understanding individual dust mineralogy is also important for understanding reactivity!

Changed the following sentence to:

These example spectra of transported dust should also be useful for studies of ice nucleation, radiative properties, and in-homogeneous processes of dust,

Fig. 1: Explaining the color code for the ions in the caption would be useful.

Color code now included.

Fig.2: Should cite your prior paper in the caption where this method was developed so the connection is clear.

Citation now included.

Fig. 4: The phosphate marker I mentioned above for biological is evident here, why is it not also used? Granted there are mineral sources of phosphate, but it could be used in combination with CN- and CNO-.

See discussion on in-organic phosphate above.

Fig. 6: I could not find the point for pure quartz. Explain in caption that big symbols are for reference samples, and make the symbol line thicker so they are easier to see. Also add the sample name to the top of each plot as in Fig. 7.

This figure has been updated as suggested.

Fig. 7: Please explain what this means: "The color function is proportional to the Tau parameter of crystal structure which is also displayed as a histogram"

The caption has been updated:

The color function is proportional to the τ parameter as defined by the crystal structure analysis technique. The distribution of τ for each sample is also displayed as a histogram (d, h).

Fig. 10: Hard to see symbols. Make lines thicker and use a different color.

The symbols have been changed.

References: Many cite the ACPD version instead of the ACP one. Please correct.

Corrected

Pg 2/line 21: "affects" not effects

Corrected

Interactive comment on “Mineralogy and mixing state of North African mineral dust by on-line single-particle mass spectrometry” by Nicholas A. Marsden et al.

Detailed Response to Anonymous Referee #2

Reviewer's comments in black

Authors' response in blue

Changes to the manuscript in green

Major comments: I would like to see more discussion of uncertainties in these measurements. In particular, the manuscript mentions that the LAAPTOF instrument tends to undercount silicate particles (page 12, line 13). Is there any evidence that it could undercount selectively and thus introduce a bias into the results as presented? In other words, are there any chemical biases in the way LAAPTOF detects silicate-rich particles?

There is certainly evidence that the instrument undercounts selectively, and We do have a sentence in the results section of the ambient measurement that alludes points out the temporal evolution is more important than the number counts.

Note that these fractions are relative to the detection efficiency of the instrument to each particle type, but the temporal evolution is representative.

However, we agree that it is not explicit what impact this has on the data. We have added the following paragraph to the Methods Section 2.1 to summaries what we know about the selectivity of the techniques regarding mineral types:

Laboratory evaluation of the fiber-coupled laser system indicate that the detection efficiency peaks at 0.25 with spherical particles \cite{Marsden2016a}, but the overall efficiency of the instrument also depends on ablation efficiency with respect to particle composition. In a study of nominally pure mineral samples, \cite{Marsden2017} reported the number of optically detected particles that produced a mass spectra (i.e. ablation efficiency or hit rate) of 0.29 and 0.14 for illite and kaolinite respectively, but was also dependent on the amount of impurities such as Titanium. Furthermore, from the authors own experience, it likely that pure quartz may have an ablation efficiency close to zero and is not considered in our analysis, but is unlikely to be a major component in the fine fraction in any case. The potential maximum overall efficiency of the LAAPTOF measurement of clay mineral ranges from 0.0725 for pure spherical particles particles of illite, to 0.035 for pure spherical particles of kaolinite. The exact efficiency of the instrument is not known in most situations because the size, shape and composition of the particles would have to be known a priori for accurate calibration.

We also now make it clear in the first paragraph of the Conclusions that the measurements do not provide complete quantitative coverage of the mineralogy of all mineral dust:

Despite the fact that the technique provides incomplete coverage in terms of particle number, elemental composition, and mineralogy; it was possible to clearly detect regional differences in the mineralogy in single particles of suspended soil and ambient transported dust.

And later in the conclusion we add the following for emphasis:

Although semi-quantitative in terms of particle number fractions due to number counting bias effects associated with instrument function, the relative temporal trends are very informative.

In the analysis of dust mixing state, chlorine, CN- and CNO- (termed “org-bio”) and sulfate (later nitrate) were chosen as mixing state markers. Comparing between soils collected from the ground and particles analyzed in-situ for these particular components is complicated because of atmospheric processing, but the text seems to draw an equivalence here. For example, CN- and CNO- might indicate a biological or biogenic fraction for soils, but in situ they are much more likely to arise during atmospheric processing and using them as biological markers leads to large overestimates. Similarly, the large chlorine fractions at Cabo Verde are largely expected because of marine influence at that sampling location, but their origin is likely very different in the laboratory soils collected in-land.

We totally agree. It was not our intention to draw equivalence, but to point out that mineral dust particles are already mixed before emission and transport. The text failed to do that explicitly. We have added the following to the Results/Discussion *Section 3.3 Temporal evolution of the mixing state of silicate particles (ICE-D)*
The mixing of silicate and non-silicate within single particles may result from processes within the native soil (primary), or during atmospheric transport (secondary). The analysis of the suspended soil dust (INUIT09) shows mineral particles in North African soils are already mixed, particularly with varying quantities of chlorine, sulphate and organic/biological material.

We think the nitrate mixing has a large influence from the atmosphere due to the low level of variation in the soil compared to the ambient measurements. We have added to the conclusions:

Internal mixing state was of some use to understanding transport history of ambient dust, but must be used with caution because some degree of mixing was already present in the primary soil. However, variations in internally mixed nitrate suggested dust from the NW margins of the Sahara was deposited into the marine boundary layer after transport in the Saharan air layer.

Minor comments: In section 2.1.1, large parts of the text (especially first two paragraphs read like introductory material instead of methods.

Agreed. We have moved the description of the crystal structure of the common minerals to the introduction.

Page 8, line 17: Figure 6 is called out in the text before Figures 4 or 5.

This has been corrected.

General comment for the methods section: please indicate the number of single particles analyzed in laboratory and field studies.

The number of particles has been added to the captions where appropriate.

Results, first sentence: “. . . we choose to analysis . . .

” should be we chose to analyze? Please clarify.

The sentence no longer contains this sentence as it is already covered in the Methods section.

Section 3.1, line 12: the authors say that vast majority of particles contained silicate markers, but then they also say that all particles contained some silicate minerals. This is a bit vague.

This sentence has been removed. The first paragraph of the Results section now gives an overview of the particle size distribution of the suspended dust, and the coverage of the two techniques. This was in response to comments from the other reviewers.

Page 11, lines 2-5: I am not sure I follow the reasoning here and in Figure 8. For the Moroccan sample, the two techniques seem to be showing the exact opposite composition.

This was not well explained in the body text or the caption. We have re-written the body text to the following:

A comparison of the sub-composition $(Al+Si)/(Al+Si+K+Na)$ obtained by SPMS and SEM measurement (Fig. \ref{SEM_SPMS}) demonstrates a much greater sensitivity to alkali metals in the SPMS measurement (due to low ionisation energy) than in the established filter technique. The SEM techniques show a lower $(Al+Si)/(Al+Si+K+Na)$ ratio in the Moroccan sample (DDS01, panel (a)) compared to the Sahel sample (SDN02, panel (C)), but this is greatly exaggerated in the SPMS analysis (panels (b) and (d)) due selective ionisation of K and Na and the matrix effect.

And the caption to Figure 8:

A comparison of the relative sensitivity of the SPMS and SEM techniques to the principal elements in silicate minerals. Histograms represent the sensitivity to alkali metals of the interstitial complex with respect to the Al and Si of the silicate structure $((Al+Si)/(Al+Si+K+Na))$ in single particles. Moroccan soil sample DDS01 (a, b) compared to Sahelian soil sample SDN02 (c, d) using the SEM and SPMS technique respectively.

Section 3.2, line 9: Why were peaks shifted in positive and not negative spectra?

Peaks shifted in both positive and negative ion modes. It was just the positive mode where the shift was greater than 0.5da, and hence affected unit mass assignments.

Page 15, line 10: “Sub-compositional analysis is a techniques” – should be technique.

Corrected!

Mineralogy and mixing state of North African mineral dust by on-line single-particle mass spectrometry.

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Abstract. The mineralogy and mixing state of dust particles originating from the African continent influences climate and marine ecosystems in the North Atlantic due to its effect on radiation, cloud properties and biogeochemical cycling. ~~Single-particle mineralogy and mixing state is particularly important in many processes but is difficult to predict~~ However, these processes are difficult to constrain because of large temporal and spatial variability, and the lack of in-situ measurements of dust properties ~~during emission, transport and deposition at all stages of the dust cycle~~. This lack of measurements is in part due to the remoteness of potential source areas (PSA) and transport pathways, but also because of the lack of an efficient method to report the mineralogy and mixing state of single particles with a time resolution comparable to atmospheric processes, ~~which may last a few hours or less~~. Measurements are equally challenging in laboratory simulations where dust particles need to be isolated and characterised in low numbers whilst conditions are dynamically controlled and monitored in real time. This is particularly important in controlled expansion cloud chambers (CECC) where ice nucleating properties of suspended dust samples are studied in cold and mixed phase cloud conditions.

In this work, the mineralogy and mixing state of the fine fraction ($< 2.5\mu\text{m}$) in laboratory suspended dust from ~~the Sahara and Sahel~~ PSA in North Africa were made using novel techniques with on-line single-particle mass spectrometry (SPMS) and traditional off-line scanning electron microscopy (SEM). A regional difference in mineralogy was detected, with material sourced from Morocco contained a high number fraction of illite like particles in contrast to Sahelian material which contains potassium and sodium depleted clay minerals like kaolinite. Single-particle mixing state had a much greater local variation than mineralogy, particularly with respect to organic/biological content. Applying the same methods to ambient measurement of transported dust in the marine boundary layer at Cabo Verde in the remote North Atlantic enabled the number fractions of illite/smectite clay mineral (ISCM), non-ISCM, and calcium containing particles to be reported at a 1 hour time resolution over a 20 day period ~~alongside internal mixing~~. Internal mixing of silicate particles with nitrate, ~~sulphate-chlorine~~ and organic/biological material. ~~The ISCM and nitrate content was found to change significantly between distinct dust events, indicating a shift in source and transport pathways which may not be captured in off-line composition analysis or remote sensing techniques~~ was also measured and compared to that in the suspended soils.

The results show SPMS and SEM techniques are complimentary and demonstrate that SPMS can provide a meaningful ~~high-resolution~~ high-resolution measurement of single-particle mineralogy and mixing state in laboratory and ambient conditions. In most cases, the ~~mineralogy varies continuously between particles~~ difference in mineralogy between particles within a soil sample was continuous, rather than a collection of particles with discrete mineral phases. ~~These techniques will be useful in resolving the complexity of mineral dust transport and in obtaining atmospherically relevant test material for laboratory experiments of dust properties~~ In ambient measurements, the ISCM and nitrate content was found to change significantly between distinct dust events, indicating a shift in source and transport pathways which may not be captured in off-line composition analysis or remote sensing techniques.

Copyright statement. TEXT

10 1 Introduction

Aeolian dust derived from sources in North Africa has a substantial impact on the climate and ecosystems in the North Atlantic but our ability to simulate climate response is poor (Evan et al., 2014; Kok et al., 2018). During aeolian transport, mineral dust influences many atmospheric processes, many of which are a function of mineralogy as well as particle size and elemental composition (Formenti et al., 2011). In addition, deposition of terrestrial material into the North Atlantic ocean is important to the biogeochemical cycle of marine ecosystems as it represents a major source of iron, nitrogen and phosphorous ~~(Baker et al., 2003)~~ (Baker et al., 2003; Jickells et al., 2005).

In recent years, the composition of dust has attracted extra attention because mineral phase is thought to influence the ice nucleating (IN) ability of single particles (Zimmermann et al., 2008; Connolly et al., 2009; Möhler et al., 2008; Cziczo et al., 2009; Nieder therefore influences climate by changing the radiative properties of ice and mixed phase clouds (Rosenfeld et al., 2001; DeMott, 2003), which represent some of the biggest uncertainties in weather and climate change prediction (DeMott et al., 2010; Carslaw et al., 2013). The mechanisms involved are not well understood and many analytical techniques have been developed to help further our understanding of this important single particle process (Hoose and Mohler, 2012; Hiranuma et al., 2015). Recently, it has been demonstrated that mineral phase has an influence on heterogeneous freezing temperature, with some feldspar group minerals proving to be particularly efficient ice nucleating particles (INP) in droplet freezing experiments with nominally pure laboratory prepared mineral samples (Atkinson et al., 2013; Harrison et al., 2016; Peckhaus et al., 2016).

To complicate things further, cloud chamber studies of silicate mineral dust coated with secondary sulphate and organics have demonstrated that this mixing can alter hygroscopicity and change the ice nucleation efficiency of a particle but is dependent on the ice forming mechanism (Möhler et al., 2008; Sullivan et al., 2010a, b; Niedermeier et al., 2011; Reitz et al., 2011). In addition, laboratory studies have suggested that the internal mixing state, particularly metal oxide - clay mineral assemblages, has important influence on direct radiative properties of dust (Nousiainen et al., 2009; Jeong and Nousiainen, 2014; Kempainen et al., 2015). This highlights the need for measurement of single-particle composition, including both mineralogy and internal mixing state.

but is extremely challenging in natural dust particles due to complex mineralogy and mixing state that is a product of the source area, emission mechanism, and atmospheric processing.

Major dust emission occurs in sparsely vegetated arid areas, but only when the surface properties and meteorological conditions are favorable (Knippertz and Todd, 2012), which can be difficult to predict in dust emission models (Heinold et al., 2013). During the summer months in North Africa, the process of dust advection is associated with moist convection (Schepanski et al., 2009b) and results in a complex structure of stratified layers of warm dry air with very high dust concentrations (Dunion and Marron, 2008). Satellite ~~observation~~ observations show that these layers can be transported westward in discrete plumes ~~thousands of miles westwards~~ over the Atlantic Ocean towards the Caribbean basin (Kaufman et al., 2005; Zhu et al., 2007; Doherty et al., 2008; Tsamalis et al., 2013).

The source of these dust plumes ~~is~~ are arid soils that consist of a complex mixture of organic and inorganic material. The inorganic material largely consists of ~~silicates~~ (Quartz)silicate minerals (quartz, feldspars, clay minerals), carbonate and metal oxides that occur as whole grains or mixed mineral phases. The abundance of mineral ~~types~~ phase has a strong grain size dependence, with quartz occurring in the coarse fraction and clay minerals dominating the fine fraction, but the size distribution is modified during emission (Perlwitz et al., 2015a) ~~so that the source soil,~~ so that ratios of mineral phases in the lofted mineral dust aerosol may not be completely representative of ~~the lofted mineral dust aerosol~~ that of the source soil. Aircraft observations have demonstrated that the size distribution of dust plumes also evolve during transport which ~~effects~~ affects optical properties (Ryder et al., 2013), but the contribution from associated changes in composition are not understood.

~~High temporal resolution measurements of dust mineralogy~~ Measurements of ambient dust properties are needed to inform ~~accurate~~ simulations of dust emission, transport and deposition processes in ~~the present day and in the paleoclimate~~ present day climate and paleoclimate models. For example, the provenance of mineral dust has been determined by comparing mass fraction ratios of ~~mineral types~~ certain mineral phases to the bulk analysis of soils in potential source areas (PSA) (Caquineau et al., 2002; Scheuven et al., 2013). Although improved soil maps are available for North Africa (Claquin et al., 1999; Nickovic et al., 2012; Journet et al., 2014), they still lack the spatial resolution required to represent the heterogeneity of soil within a PSA and results in an over simplification of the mineralogical relationships in a given soil type (Scanza et al., 2015). Improvements to emission simulations require validation measurements of size resolved dust mineralogy and mixing state at varying distances from the source (Perlwitz et al., 2015b).

Identification of the source of transported dust is problematic due to the inhomogeneity of source sediments and the mixing of material during transport. Nevertheless, analysis of bulk mineralogical composition of source sediments can provide markers, with illite/kaolinite ratios being particularly useful (Caquineau et al., 2002). At the Cabo Verde Islands, Glaccum and Prospero (1980) analysed day long exposures of filters during the summer of 1974 and concluded that illite and mica were the dominant mineral types deposited in the tropical North Atlantic. In contrast, Kandler et al. (2011a) reported kaolinite as the dominant mineral type and attributed this to the dominance of sources in the Sahel during the summer.

~~In recent years, the composition of transported dust has attracted extra attention because mineralogy is thought to influence the ice nucleating (IN) ability of single particles (Zimmermann et al., 2008; Connolly et al., 2009; Möhler et al., 2008; Cziezo et al., 2009; I therefore influences climate by changing the radiative properties of ice and mixed phase clouds (Rosenfeld et al., 2001; DeMott, 2003);~~

which represent some of the biggest uncertainties in weather and climate change prediction (DeMott et al., 2010; Carslaw et al., 2013). The mechanisms involved are not well understood and many analytical techniques have been developed to help further our understanding of this important process (Hoose and Mohler, 2012; Hiranuma et al., 2015). Recently, it has been demonstrated that mineral phase has an influence on heterogeneous freezing temperature, with some feldspar group minerals proving to be particularly efficient ice nucleating particles (INP) in droplet freezing experiments with nominally pure laboratory prepared mineral samples (Atkinson et al., 2013; Harrison et al., 2016; Peckhaus et al., 2016). However, the IN fraction in natural dust samples is much more difficult to assess due to complex mineralogy and mixing state that is difficult to resolve.

To complicate things further, cloud chamber studies of silicate mineral dust coated with secondary sulphate and organics have demonstrated that this mixing can increase hygroscopicity and lower the ice nucleation efficiency of a particle (Möhler et al., 2008; Niedermeyer et al., 2010). In addition, laboratory studies have suggested that the internal mixing state, particularly metal oxide–clay mineral assemblages, has important influence on radiative properties of dust (Nousiainen et al., 2009; Jeong and Nousiainen, 2014; Kempainen et al., 2015; Di Biase et al., 2016). This highlights the need for measurement of single particle composition, including both mineralogy and internal mixing state in order to provide better constraints for global climate models (Kok et al., 2017).

Silicates are the most important group of rock-forming minerals and comprise a huge spectrum of compositions and crystal structures. However, the fine fraction of continental soil largely consists of clay minerals with minor amounts of feldspar and quartz (Perlwitz et al., 2015b). Clay minerals are phyllosilicates which consists of 2D layers of silicon tetrahedrally co-ordinated with oxygen, and aluminum octohedrally co-ordinated with oxygen and/or hydroxyl. A simple example is that of the mineral kaolinite ($Al_2Si_2O_5(OH_4)$), in which these two layer types are repeated to form a 3D structure referred to as 1:1 layer structure (Fig. 1(a)).

A more complicated structure results in the presence of large cations of potassium, sodium and calcium. The charge and ionic radius of these cations is accommodated in a separate sheet of interstitial cations that must be charge balanced by the tetrahedral and octohedral layers. In the case of potassium, charge balance is achieved with the common 2:1 layer structure of illite ($K_{1.5-1.0}Al_4[Si_{6.5-7.0}Al_{1.5-1.0}O_{20}](OH_4)$) in which there are two tetrahedral layers for each octohedral layer (Fig. 1(b)). These types of clay mineral are expected to be abundant in Saharan dust. For example, in a previous study using transmission electron microscopy (TEM) of sliced dust particles collected at the island of Tenerife in the North Atlantic, the majority of particles of transported Saharan dust were clay rich agglomerates primarily composed of a matrix of illite/smectite clay minerals (ISCM) with inclusion of kaolinite and hematite (Jeong et al., 2016).

The feldspar group of minerals are chemically similar to the clay minerals but a higher atomic content of alkali and alkaline earth metals demands a different crystal structure to achieve charge balance. In K-feldspars ($K[AlSi_3O_8]$), such as microcline and orthoclase, interstitial cations of potassium are fixed in a cavity where they are charge balanced by a 3D network of tetrahedrally co-ordinated silicon and aluminum (Fig. 1(c)). Whilst these minerals are expected to be less common than clay minerals in fine mineral dust, they may be particularly important in ice nucleation in the atmosphere.

The analytical challenge arises from the fact that common mineral phases are very similar in composition, and undergo significant alteration and weathering in the soil making pure minerals difficult to identify (Formenti et al., 2014). For example, in clay minerals, potassium, sodium and calcium are interchangeable during the weathering process so that composition is not

necessary uniform throughout the crystal lattice. Indeed, the illite structure in Fig. 1(b) is the idealised version of the pure mineral, which is often referred to as an end-member of the illite series. Complete uniformity of clay mineral composition is unlikely on the scale of a single particle or between particles from the same soil sample.

5 In order to identify the mineral phases present, one must either make an accurate quantitative measurement of the elemental composition or make an analysis of crystal structure. An established approach to both ambient and laboratory measurements is to collect particles on filters and impactors for subsequent off-line analysis. Bulk mineralogy can be obtained with crystal structure analysis by X-ray diffraction (XRD), and the composition of individual particles is assessed by advanced microscopy. Scanning Electron Microscopy (SEM), often combined with energy-dispersive X-ray spectrometry (~~EDXS~~is a favored EDX), is a powerful method for elucidating composition because of the ability to probe the composition of individual ~~partieles~~.
10 ~~However, there are a number of drawbacks to this approach including; labor intensive post sampling analysis, dust particles.~~ The application of these techniques can differentiate silicate from calcium rich particles and show evidence of heterogeneous reactions in the atmosphere (Ro et al., 2005; Jeong and Chun, 2006; Sobanska et al., 2012).

However, further differentiation of silicate mineral phase in single particles is hampered by the difficulty in leveraging the full quantitative capability of SEM due to particle morphology effects, ~~and loss of temporal resolution in dynamic situations.~~ Consequently, ~~small number of partieles are silicate particles are often~~ reported in compositional groups, ~~such as the frequently used scheme described by Kandler et al. (2009),~~ which describes the dominant elemental features but not ~~mineralogy; actual mineral phase (Kandler et al., 2009; Hammer et al., 2018).~~ In addition, ~~there are a number of drawbacks to this off-line approach including; labor intensive post sampling analysis, and loss of temporal resolution in dynamic situations.~~
15 However, further differentiation of silicate mineral phase in single particles is hampered by the difficulty in leveraging the full quantitative capability of SEM due to particle morphology effects, ~~and loss of temporal resolution in dynamic situations.~~ Consequently, ~~small number of partieles are silicate particles are often~~ reported in compositional groups, ~~such as the frequently used scheme described by Kandler et al. (2009),~~ which describes the dominant elemental features but not ~~mineralogy; actual mineral phase (Kandler et al., 2009; Hammer et al., 2018).~~ In addition, ~~there are a number of drawbacks to this off-line approach including; labor intensive post sampling analysis, and loss of temporal resolution in dynamic situations.~~

A second, but less common approach is to use single-particle mass spectrometry (SPMS) to provide an on-line assessment
20 of ~~the aerosol~~ composition. An advantage is that the high temporal resolution allows the evolution of the particle composition to be measured in a dynamic setting (Cziczo et al., 2006; Zelenyuk et al., 2009; Gaston et al., 2013), and the instruments can be deployed in-line with other techniques such as counterflow virtual impactor (CVI) to measure ice residuals (Cziczo et al., 2003; Gallavardin et al., 2008; Baustian et al., 2012; Zelenyuk et al., 2015; Worringen et al., 2015; Schmidt et al., 2017). However, compositional analysis with SPMS is fraught with difficulties relating to poor reproducibility, and the non-quantitative nature
25 of the measurement associated with instrument function and particle matrix effects (Reilly et al., 2000; Sullivan and Prather, 2005; Murphy, 2007; Hatch et al., 2014). ~~These problems are particularly problematic for the analysis of irregular shaped particles composed of mineral phases whose elemental composition are similar. Consequently, SPMS has-~~

The matrix effects arise from the incomplete desorption and ionisation process and the subsequent competitive ionisation of atoms and molecular fragments, so that co-variance of analyte signals is relative to ionisation energy and electron affinity of the surrounding matrix (Reinard and Johnston, 2008). In circumstances where the composition of the matrix is known a priori, careful calibration with a suitable proxy can produce quantitative or semi-quantitative measurements of an analyte within a single particle (Gross et al., 2000; Bhave et al., 2002). However, if the particle matrix is complex, such as in soils and transported dust, this type of calibration cannot be made due to the lack of a suitable proxy.
30 The matrix effects arise from the incomplete desorption and ionisation process and the subsequent competitive ionisation of atoms and molecular fragments, so that co-variance of analyte signals is relative to ionisation energy and electron affinity of the surrounding matrix (Reinard and Johnston, 2008). In circumstances where the composition of the matrix is known a priori, careful calibration with a suitable proxy can produce quantitative or semi-quantitative measurements of an analyte within a single particle (Gross et al., 2000; Bhave et al., 2002). However, if the particle matrix is complex, such as in soils and transported dust, this type of calibration cannot be made due to the lack of a suitable proxy.

Despite these limitations, SPMS can characterise a particle population by classifying particle types and measuring temporal trends in particle number concentrations using cluster analysis (Hinz et al., 2006; Rebotier and Prather, 2007; Gross et al., 2010).
35 Despite these limitations, SPMS can characterise a particle population by classifying particle types and measuring temporal trends in particle number concentrations using cluster analysis (Hinz et al., 2006; Rebotier and Prather, 2007; Gross et al., 2010).

Although the reported number concentration are also not fully quantitative (Murphy, 2007), a relative trend in certain particle types can be achieved. This techniques have been used to discriminate mineral dust particles from other refractory aerosol types such as sea salt (Sullivan et al., 2007b; Dall'Osto et al., 2010; Fitzgerald et al., 2015; Schmidt et al., 2017), but not differentiate mineralogy- (Sullivan et al., 2007a; Dall'Osto et al., 2010; Fitzgerald et al., 2015; Schmidt et al., 2017), but cannot differentiate the actual mineral phase of silicates within dust particles. More recently, a machine learning technique has shown promise with the classification of mineral dusts of similar composition (Christopoulos et al., 2018), but this techniques also requires suitable mineral dust proxies for training data.

In this study, a modified laser ablation aerosol particles time of flight (LAAPTOF) a previous study using a single particle mass spectrometer (LAAPTOF, AeroMegt GmbH) was used to evaluate the composition of laboratory suspended soil, and ambient transported dust in the remote North Atlantic. A method for describing particle mineralogy and mixing state using sub-compositional analysis is introduced and demonstrated with nominally pure mineral samples. We applied this method, Marsden et al. (2018) presented a novel method for the assessment of single crystal structure that, when used in tandem with the more typical elemental composition measurement, performed an on-line differentiation of single particles of kaolinite, illite and K-feldspar mineral phases. In the present study, we applied a refined version of these techniques to suspended natural soils sampled from two PSA in North Africa, sampled at the Aerosol Interactions and Dynamics in the Atmosphere (AIDA) facility at the Karlsruhe Institute of Technology (KIT), as part of the ice nucleation research unit (INUIT) program studying heterogeneous ice formation in the atmosphere (<https://www.ice-nuclei.de/the-inuit-project/>). These results are The results of analysing soil from PSAs in North Africa were used to interpret ground based ambient measurements of transported dust using a LAAPTOF at Cabo Verde at Praia, Cabo Verde in the tropical North Atlantic during the summer of 2015 as part of the Ice in Clouds Experiment- Dust (ICE-D) campaign.

2 Methods

In order to characterize North African mineral dust aerosol, we compared laboratory suspended soil samples collected from PSAs in North Africa during the INUIT09 campaign, with ambient measurements of transported dust in the marine boundary layer (MBL) at Cabo Verde in the tropical North Atlantic during the ICE-D experiment. In order to make this comparison, we introduce reproducible methods of describing the mineralogy and mixing state of single dust particles extracted from suspension using crystal structure and sub-compositional analysis with a LAAPTOF instrument. These techniques A limited number of mineral phases were chosen to create fingerprints to which the more varied mineralogy of naturally occurring sediments could be compared. Nominally pure samples of illite, Na-montmorillonite, kaolinite; along with orthoclase (K-feldspar), plagioclase (Na-feldspar) were used to represent the end members of the clay minerals and feldspar groups respectively, based on the assumption that the fine fraction ($< 2.5\mu\text{m}$) continental sediment is primarily composed of aluminosilicate clays and feldspars. Quartz and carbonate minerals are not considered with sub-compositional analysis due to the inability of the LAAPTOF to efficiently ablate pure quartz and the apparent lack of a clear carbonate signal respectively. In ambient dust,

calcium rich particles are considered separately to aluminosilicate particles after being separated using traditional cluster analysis techniques.

The LAAPTOF instrument and data analysis methods are described below, along with ~~SEM-EDXS SEM-EDX~~ methods used to obtain elemental composition of the laboratory suspended dust for method validation. The experimental setup of the
5 INUIT09 laboratory campaign and ICE-D ~~measurement experiments~~ ambient measurement are also described in this method section.

2.1 LAAPTOF Single particle mass spectrometry

In a previous study, Shen et al. (2018) showed that the LAAPTOF single particle mass ~~spectrometry (SPMS)~~ spectrometer is capable of distinguishing the composition of different particles in the ambient environment using a combination of fuzzy
10 clustering and reference based spectra classification, whilst Ahern et al. (2016) demonstrated a positive correlation between ion signals of organic markers and the quantity of condensed organic coating, despite inhomogeneity in the soot core of the particles. These studies show that the LAAPTOF is an appropriate platform for studying the composition and internal mixing state of refractory aerosol.

In SPMS, aerosol is directly introduced into the instrument via a pumped inlet so that sample collection and preparation are
15 not required. Particle composition is analysed by time-of-flight mass spectrometry (TOFMS) after laser desorption ionisation (LDI) of individual particles using a high powered UV laser. The LAAPTOF instrument features an aerodynamic lens inlet, optical particle detection, LDI ion source and bipolar TOFMS as previously described by Gemayel et al. (2016). ~~The instrument is capable of providing size resolved composition measurements in the size range approx. 0.4–2.5 μm. The instrument used in this investigation features a particle detection system based on a fibre-coupled laser delivery that allows the simple interchange~~
20 ~~of laser systems of different wavelengths.~~ Within the instrument, LDI ~~was is~~ performed by ArF excimer laser (model EX5, GAM Laser Inc.), set to deliver 3-5mJ/pulse of 193nm radiation with a pulse width of 8ns.

~~The SPMS technique~~ Like all single particle mass spectrometers, the LAAPTOF measurements is subject to a number of ~~measurements biases with regard to particle size, shape and composition~~ biases that result in preferential transmission, detection and ablation efficiencies of certain particles (Murphy, 2007). ~~Table 1 documents differences in instrument~~ The instrument
25 used in this investigation features a modified particle detection system based on a fibre-coupled laser delivery that allows the simple interchange of laser systems of different wavelengths. The instrument is capable of providing size resolved composition measurements for up to 200 particles per second in the size range approx. 0.4 – 2.5 μm, but the actual detection efficiency of particles within this range depends on the size, shape and composition, as well as the wavelength of the optical detection system. Differences in instrument setup between the laboratory and ambient measurements that may impact the comparison of
30 the two ~~datasets. For a detailed review of how these phenomena affect the LAAPTOF measurements, the reader is referred to Marsden et al. (2016) and references therein.~~ data sets are presented in Supplement S1.

~~LAAPTOF setup parameters that differ between the laboratory and ambient acquired datasets~~ Parameter Laboratory Ambient
0.5exAerodynamic Sizing no yes Detection laser wavelength 488 532 Excimer pules energy 4mJ 3mJ Signal line attenuation
high low Laboratory evaluation of the fiber-coupled laser system indicated that the peak detection efficiency is 0.25 with

spherical particles Marsden et al. (2016), but the overall efficiency of the instrument also depends on ablation efficiency with respect to particle composition. In a study of nominally pure mineral samples, Marsden et al. (2018) reported the number of optically detected particles that produced a mass spectra (i.e. ablation efficiency or hit rate) of 0.29 and 0.14 for illite and kaolinite respectively, but was also dependent on the amount of impurities such as Titanium. Furthermore, from the authors own experience, it likely that pure quartz may have an ablation efficiency close to zero and is not considered in our analysis, but is unlikely to be a major component in the fine fraction in any case. The potential maximum overall efficiency (detection efficiency * ablation efficiency) of the LAAPTOF measurement of clay mineral ranges from 0.0725 for pure spherical particles particles of illite, to 0.035 for pure spherical particles of kaolinite. The exact efficiency of the instrument is not known in most situations because the size, shape and composition of the particles would have to be known a priori for accurate calibration.

In a previous study, Shen et al. (2018) showed that the LAAPTOF is capable of distinguishing the composition of different particles in the ambient environment using a combination of fuzzy clustering and reference based spectra classification, whilst Ahern et al. (2016) demonstrated a positive correlation between ion signals of organic markers and the quantity of condensed organic coating, despite inhomogeneity in the soot core of the particles. These studies show that the LAAPTOF is an appropriate platform for studying the composition and internal mixing state of refractory aerosol.

2.1.1 Crystal structure analysis of silicates

Silicates are the most important group of rock-forming minerals and comprise a huge spectrum of compositions and crystal structures. However, the fine fraction of continental soil largely consists of clay minerals with minor amounts of feldspar and quartz (Perlwitz et al., 2015b). Clay minerals are phyllosilicates which consists of 2D layers of silicon tetrahedrally co-ordinated with oxygen, and aluminum octohedrally co-ordinated with oxygen and /or hydroxyl. A simple example is that of the kaolinite, in which these two layer types are repeated to form a 3D structure referred to as 1:1 layer structure (Fig. 1(a)). A more complicated structure results in the presence of large cations of potassium, sodium and calcium. The charge and ionic radius of these cations is accommodated in a separate sheet of interstitial cations that must be charge balanced by the tetrahedral and octohedral layers. In the case of potassium, charge balance is achieved with the common 2:1 layer structure of illite (Fig. 1(b)) in which there are two tetrahedral layers for each octohedral layer.

In theory, these structures are free to polymerise uniformly in 2 dimensions. However, this is rarely realised because potassium, sodium and calcium are interchangeable as interstitial cations so the composition is not necessary uniform throughout the crystal lattice. Indeed, the illite structure in Fig. 1(b) is the idealised version of the pure mineral, which is often referred to as an end-member of the illite series. Complete uniformity of clay mineral composition is unlikely to exist and on the scale of a single particle or between particles from the same soil sample.

Larger and more uniform crystals of feldspars are more common due to their formation from molten material rather than through the alteration of other minerals as is the case for clay minerals. In K-feldspar, such as microcline and orthoclase, interstitial cations of potassium are fixed in a cavity where they are charge balanced by a 3D network of tetrahedrally co-ordinated silicon and aluminum (Fig. 1(c)). Substitution of potassium, sodium and calcium is not readily achieved in the solid phase like the clay minerals, but dissolution of these cations results in alteration of feldspar to clay minerals during

~~diagenesis of sediments. For example, K-feldspar can be progressively altered to form quartz and kaolinite if the potassium is removed by dissolution.~~

In a study of ion formation mechanism, Marsden et al. (2018) showed that the ionisation potential and co-ordination of interstitial cations has a strong influence on how the crystal structure breaks apart during LDI process of silicate particles. This is exploited for the differentiation of mineral phase by the measurement of average ion arrival of the O^- and SiO_3^- ion species, which is thought to record the initial kinetic energy of the ionic fragments during ablation.

~~Expressed as a peak shift ratio (τ), which can be compared~~ With this technique we can compare the structure of soil dust samples to nominally pure mineral samples on a particle by particle basis, ~~laboratory~~. Laboratory calibrations have demonstrated that for ~~illite-smectite clay minerals (ISCM)~~ ISCM the abundance of exchangeable sodium and potassium cations results in a unique range of τ values between 0.2-0.58. Feldspars typically produce τ values >0.58 (Fig. 2) due to the interlocking nature of the interstitial cation in their crystal structure. Kaolinite and amorphous glass produces τ values close to 1 due to the complete absence of interstitial cations and lack of crystal structure respectively.

2.1.2 Sub-compositional analysis of silicates

Sub-compositional analysis is ~~used to produce relative composition measurements that can be compared to fingerprints generated from nominally pure mineral samples. Silicate composition is considered with the~~ a technique that is commonly used for the analysis of complex chemical relationships in circumstances in which the full composition of a substance is impossible to obtain, such as in whole-rock geochemical analysis (Pawlowsky-Glahn and Egozcue, 2006), where it is convenient to describe the composition in terms of a relative measurement of carefully chosen components. The ternary diagram provides an intuitive way of displaying relative information whilst avoiding some of the sub-compositional incoherence associated with two component systems. The technique has been applied to the single particle analysis of natural Asian mineral dust using SEM (Yuan et al., 2004), and transported Asian dust using SPMS (Sullivan et al., 2007a). It is particularly well suited to SPMS because the composition obtained from the mass spectra is inherently sub-compositional due to the matrix effect.

Sub-compositional analysis was used to produce fingerprints of pure mineral phases using the ternary system $Al^+ + Si^+, K^+, Na^+$ ~~which represents the~~ cations readily observed in the SPMS of mineral dust (m/z 27, 28, 39, 23 respectively). ~~The K^+ signal is a useful reference as its ionization energy is the lowest of the common cation signals, meaning it is less likely to be perturbed by the presence of other elements. This approach differs from the Ca^+, Fe^+, Al^+ ternary system used by Sullivan et al. (2007b) which could be significantly perturbed by variations in K^+ and Na^+ due to the matrix effect. In addition, Ca^+ is not considered due to problems differentiating this signal from the potassium signal at m/z 39—40, and the potential for interference from calcium within carbonate minerals.~~

Source clay material from the clay mineral society and crushed feldspar crystals were suspended in a home made dust tower in the experiment described in Marsden et al. (2018). ~~The samples were representative of the end-members of the clay minerals and feldspars with varying alkali metal content.~~ Elemental composition and mineralogy of these samples have been previously characterised and can therefore be used as reference fingerprints for comparison with ~~uncharacterised~~ natural soil. Ternary diagrams of the clay minerals and feldspar standards are displayed ~~in Fig separately in Fig.~~ 3.

~~Although the measurement is clearly non-quantitative with respect to bulk XRF analysis, the relative measurement produces a clear separation between the clay minerals, and between K and Na rich feldspars.~~

The 2D space in these diagrams are ~~also non-linear~~ and due to the matrix effect, ~~so that a fully~~ quantitative composition cannot be deduced from these plots alone. ~~Consequently, clay minerals and feldspars are not easily distinguishable from each other despite differences in actual composition,~~ but it is interesting to note that K-feldspar appears less K and Na rich than illite clay despite the structural formula and ~~XRF X-ray fluorescence~~ analysis of the bulk sample indicating the contrary. This is because the tetrahedral framework of the feldspar makes the release of interstitial K^+ and Na^+ without also releasing Al^+ improbable, whereas they can be released independently of Al^+ from the weakly bonded interlayer in 2:1 clay structure.

Although the elemental sub-composition measurement is clearly non-quantitative with respect to bulk XRF analysis, the measurement is semi-quantitative (relative) with respect to samples of minerals with the same crystal structure. For example, a clear separation between K and Na rich feldspar is apparent in Fig. 3, which is relative to their actual elemental ratios. This is not true if comparing the clay mineral illite with the framework silicate K-feldspar, which would not be easily distinguishable from each other if plotted in the same space, despite the clear differences in elemental composition. It is therefore necessary to apply crystal structure analysis to achieve semi-quantitative composition and distinguish clay minerals from feldspar when analysing natural soils with SPMS.

2.1.3 Sub-composition analysis of internal mixing state

Internal mixing of non-mineral species can occur during soil formation or during transport in the atmosphere where heterogeneous reactions ~~with ozone~~ take place on the surface of the particle (Usher et al., 2003). Reactions with nitric, sulphuric and organic acids can produce nitrate, sulphate and organics on the particle surface respectively. Reference spectra obtained with the LAAPTOF during the FIN-1 campaign show the presence of sulphate marker $HSO_4(m/z97)$ on particles after mixing suspended feldspar with ozone and sulphuric acid in the AIDA chamber (Fig. 4(b)). Similarly, organic markers C_2, C_2H and $C_2H_2(m/z24, 25, 26)$ appear on particles after mixing suspended feldspar with ozone and α -pinene (Fig. 4(c)). Only small organic fragments are observed due to the extensive fragmentation of organic molecules. These ion combinations have also been observed on ambient mineral dust using SPMS instruments (Silva and Prather, 2000; Sullivan et al., 2007b; Fitzgerald et al., 2015) (Silva and

In ambient dust, organic or biological material may have been mixed with a dust particle in the soil before emission. Indeed, the transport of microorganisms in dust storms is human health concern (Griffin, 2007). Recently, Yamaguchi et al. (2012) provided direct evidence of bacterial cells on Asian dust particles and demonstrated a global dispersion pathway through dust transport. The internal mixing of biological material with dust particles is therefore of interest. LAAPTOF reference spectra of bacteria, also from the FIN-1 campaign, show strong signals of CN and $CNO(m/z26, 42)$ (Fig. 4(d)) representing fragments of nitrogen containing organic compounds. These markers have been attributed to compounds of biological origin (Pratt et al., 2009; Cahill et al., 2012; Creamean et al., 2013), although other studies have found these markers in aerosol where biological components were not expected (Sodeman et al., 2005; Zawadowicz et al., 2017; Wonaschuetz et al., 2017). Consequently, we describe these markers as organic-biological (Org-Bio hereafter).

Internal mixing of natural soil samples with non-minerals in this work are considered with the ternary sub-composition Cl^- , $CN^- + CNO^-$, SO_4^- . These markers represent compounds that could be present in soils and ambient dust, but are not present in silicate minerals structure. ~~The inclusion of the Phosphate marker PO_3^- is not considered because it could be derived from the calcium phosphate mineral apatite as well as biological material, and it therefore not a reliable indicator of mixing state. The Cl^- is important elemental ion is included despite it also having mixed provenance such as primary chlorides or secondary uptake of HCl (Sullivan et al., 2007b), because it is a non-silicate element with a preferentially ionised due to very high electron affinity and is therefore therefore is included as a reliable reference – reference that would otherwise perturb the measurement. It is also an indication of the purity of silicate particles as pure fresh silicate should not contain Chlorine.~~

2.2 Scanning electron microscopy

10 Particles were sampled from the AIDA chamber with a single-stage nozzle impactor (50% low cut-off diameter at approximately $0.1\mu m$ aerodynamic diameter; for specifications see Kandler et al. (2007)) on nickel grids (~~transition electron microscopy (TEM) TEM~~ grids type S162N9, Plano, Wetzlar, Germany). The inlet was connected to a sampling line on the AIDA chamber and the sample time varied between 12-16 min.

All samples were analysed with computer controlled scanning electron microscopy (ccSEM) using a FEI Quanta 400 FEG
15 instrument (FEI, Eindhoven, The Netherlands) equipped with an energy-dispersive X-ray detector, X-Max150 (Oxford, Oxfordshire, United Kingdom), and the Oxford software Aztec (version 3.3 SP1). An acceleration voltage of 12.5 keV, spot size 5, a working distance of 10mm and high vacuum conditions (~~+0.5 hPa~~ $10^{-5} hPa$) were used for all samples. Backscatter electron images were used to segment particles from substrate. The particles of interest were measured with 4 seconds counting time for X-ray microanalysis. The TEM grids were mounted in a copper sample holder (avoiding interference with chemical
20 composition of the particle) equipped with a beam trap (maximizing the characteristic-peak-to-background ratio).

Chemical composition of all elements with atomic number higher than 3 (Li) was determined with energy-dispersive X-ray microanalysis. ~~ZAF correction (provided by the software) was used to correct for matrix effects (atomic number effect, absorption effect and the fluorescent excitation effect).~~ A sorting step after ccSEM was performed to remove particles with low X-ray counts (due to shading effects) and features of the TEM grid. Between 159 and 776 aluminosilicates were detected per
25 samples with the highest abundance of particles at an average diameter of $200nm$.

The traditional method for reporting the composition of aerosol particles involves the classification of particles into compositional groups using a variety of elemental ratios and boundary rules e.g Kandler et al. (2007, 2011b); Young et al. (2016). However, these classification systems are impossible to apply to SPMS due the matrix effects that skews and suppresses elemental ratios. We therefore choose to display the SEM composition as ratios of Al/Si , $(K + Na)/Si$ and $(Fe + Mg)/Si$ ratios,
30 which leverages the quantitative ability to produce a representation of the interstitial cation and aluminosilicate structure that can be intuitively compared to the ternary diagrams obtained by SPMS.

The Scatterplot of single particle average chemical composition ~~of nominally pure mineral samples~~ is plotted in Fig. 5(a). This demonstrates that pure mineral can potentially be differentiated using quantitative Al/Si ratio and the $(K + Na)/Si$

(cation to silicate) ratio. For example, the pure Kaolinite clay mineral has the highest Al/Si ratios (≈ 1) but no $(K + Na)$ content. In general, the decreasing Al/Si ratio must be balanced by increasing cation/Si ratio in clay minerals.

2.3 INUIT09 Laboratory Suspended Dust Experiment

5 ~~One of the objectives of the INUIT09 campaign (July 2017) was to determine if single particle mass spectrometry is capable of differentiating between aerosol particles of different mineralogical compositions.~~

2.3.1 Experiment Setup

For the aerosol generation during the INUIT09 campaign, the natural dust samples were sieved to diameters less than $75\mu m$ and injected in either the AIDA cloud chamber or the Aerosol Preparation ~~Chamber and Characterisation~~ (APC) ~~chamber~~. For injection, a rotating brush generator linked to a cyclone impactor was used, resulting in aerosol particles with aerodynamic diameters of less than about $5\mu m$. The dust number concentration in the AIDA chamber was initially between 200 and $300cm^{-3}$ and in the APC ~~chamber~~ between 1000 and $5000cm^{-3}$. The number concentrations and size distribution of the dispersed aerosol are detailed in Supplement ~~S1S2~~.

During this study, the single particle mass spectrometer LAAPTOF was either connected to the AIDA chamber or the APC, and sampled for about 1 hour during each experiment. During the sampling time, both the AIDA chamber and APC ~~were held~~ ~~chamber were held~~ to nearly constant temperature (either $-16\text{ deg }C$ or $-21\text{ deg }C$ in AIDA and $25 - 27\text{ deg }C$ in APC) and pressure ($998 - 1010hPa$ in AIDA and $990 - 1005hPa$ in APC ~~chamber~~) conditions.

2.3.2 Soil Sampling Locations

Soil samples from two specific ecoclimatic zones were suspended at the AIDA facility; the mountainous north-west margin of the Sahara Desert, and the west-central Sahel beyond the southern margin of the Sahara Desert (here-after named Sahel Dust). These PSA were chosen because there is likely to be differences in mineralogical composition between the two zones. Analysis of surface material across North Africa are scarce, but the available studies demonstrate a North-South decrease in illite/kaolinite (I/K) ratio in the clay fraction (Caquineau et al., 2002; Scheuvens et al., 2013; Formenti et al., 2014) mainly due to differences in diagenetic history between dry and wet climate zones.

The sampling locations of the natural arid soils are displayed in Fig. 6. Moroccan dust samples were collected in the Mhamid region, on the upper Draa valley, Morocco during the Saharan mineral dust experiment (SAMUM) (Ansmann et al., 2011). The Draa valley is a large geographical feature on the Southern edge of the Anti-Atlas mountains, beyond which is the Sahara desert of Algeria. All sampling locations fall within unit 1336 in Digital Soil Map of the World (DSMW), compiled by the Food and Agriculture Organization (FAO) of the United Nations (FAO, 1995, 2007), ~~which describes the dominant soil as fluvisols (50%), associated with yermosols (20%), regosols (20%) and solonchaks (10%). DDS01~~ .

Table 1. Sampling location of natural soils for laboratory experiments

<u>Sample</u>	<u>Location</u>	<u>Notes 0.5ex>0.5ex</u>
<u>DDS01</u>	29.83773 °N, -5.76143 °E River sediments DDS02	<u>River sediments</u>
<u>DDS02</u>	29.84957 °N, -6.01508 °E	Hamada with large amounts of dust DDS03
<u>DDS03</u>	29.86202 °N, -6.156760°E	Border of dry salt/ silt plain of Lae Iriqui close to sand dune fields
<u>SDN02</u>	<u>13.516667 °N, 2.633333 °E</u>	<u>Banizoumbou, Niger</u>
<u>SDN05</u>	<u>13.522203 °N, 2.133011 °E</u>	<u>Grand Mosque, Niamey, Niger</u>
<u>DDA01</u>		<u>Dano, Burkina Faso</u>

*Signal line attenuation changes the saturation and limit of detection of the ion detection system

The samples of Sahel soil were collected from diverse geographical locations in Niger and Burkina Faso. All three sampling locations fall within the zone of kaolinite rich soil (Fig. 6) where the DSMW indicates ~~CEC~~ cation exchange capacity (CEC) <35 cmol/kg. **SDN02**

~~13.516667 °N, 2.633333 °E Banizoumbou, Niger SDN05 13.522203 °N, 2.133011 °E Grand Mosque in Niamey, Niger~~
5 ~~DDA01 Dano, Burkina Faso~~

2.4 Ambient Measurement at Cabo Verde during ICE-D

The Cabo Verde archipelago is a favorable location for remote marine measurements. Situated some 800km off the West coast of North Africa (Fig. 6), it is a site ~~of~~ at which long term measurements of greenhouse gasses, trace gasses and aerosol properties are recorded (Carpenter et al., 2010). Notable studies of mineral dust composition in the area include long term filter
10 sample collection at Cape Verde atmospheric observatory (CVAO) (Patey et al., 2015) and Praia City, Santiago Island (Salvador et al., 2016), and filter collection at Praia Airport, Santiago Island for the SAMUM campaign January-February 2008 (Kandler et al., 2011a).

Ground based ambient measurements during ICE-D took place in the mobile Manchester Aerosol Laboratory located within the perimeter of Praia International Airport, Santiago Island, Cabo Verde, (14°57'N 23°29' W, 100 m asl), approximately
15 1500m from the coast and 150m from the airport runway. The main airport terminal and the outskirts of the city of Praia were 400m and 2500m downwind of the prevailing NE wind respectively. Aerosol was sampled via a 6 inch plastic inlet fixed to a 10m tower and pumped at 185l/min. The flow was distributed to a suite of on-line instruments, including the LAAPTOF, via a system of ~~48m~~ 48mm ID lines isokinetically sampled from the main inlet, and heated to 19°C.

3 Results and Discussion

20 ~~In the analysis mineral dust, we choose to analysis the silicate mineralogy and the internally mixed non-silicate components separately using the methods described above.~~

3.1 Single particle analysis of laboratory suspended natural soil (INUIT09)

The sampling of particles took place after dispersing the source material in the APC ~~after cleaning, and it was therefore expected that all particles were particles from the original soil. Initial examination of chamber using a rotating brush generator.~~ The resulting particle concentration and size distribution is dynamic but is typically on the order of 1000cm^{-3} with a particle size mode at 200nm (See supplement S2), which is below the lower size cut of the mass spectra showed that the vast majority of particles contained the markers for silicates, indicating that all particles which produced a mass spectrum contained at least some silicate minerals. LAAPTOF, but not the filter collection. Although the two measurement techniques are not performed on the exact same particle sizes. Still, both measurements represent the fine fraction ($< 2.5\mu\text{m}$) of the dispersed dust.

3.1.1 Silicate mineralogy of laboratory suspended soil (INUIT09)

SEM EDX analysis of the suspended soil shows that the composition of single particles within each soil type varies ~~as~~ in a continuous distribution rather than in distinct clusters (Fig. 5). A distinct difference in the elemental composition of soil from the Northern Sahara and the Sahel exists in these diagrams, particularly with respect to the Al/Si ratio. The Moroccan soils (Fig. 5(b-c)) have a spread in compositions close to the illite plotted on the diagram, with the DDS01 samples being more diverse than the DDS02. In contrast, the soil from the Sahel (Fig.5(c-f)) consists of material with higher Al/Si ratio which approaches the composition of the plotted kaolinite. This is in agreement with ~~cation exchange capacity (CEC) measurements of sediments in potential source areas (PSA) -~~ CEC measurements of sediment in PSA which show that kaolinite fraction in soils increases in soils in the Southern Sahel regions compared to the northern regions of the Sahara (Scheuvs et al., 2013).

SPMS mineralogical analysis proceeds by considering the relative abundance between K , Na and $Al + Si$, which together define the phase of many minerals in the continental crust. This sub-compositional analysis was previously applied to nominally pure mineral samples from the clay mineral society (CMS) to provide a fingerprint reference for the common clay mineral phases (Fig. 4(a)). The same analysis applied to Moroccan dust (Fig. 4(a-c)) and Sahelian dust (Fig. 4(e-g)) shows key differences between the composition of the two ecoclimatic zones, with ~~Morrocan~~ Moroccan dust tending towards an illite composition and Sahelian dust tending to a kaolinite composition, in agreement with the SEM EDX analysis.

Application of the crystal structure analysis (color function in Fig. 4) to each particle indicates that the majority of the particles are of a 2:1 clay structure, even in Sahelian dust particles that have a kaolinite (1:1 clay structure) like composition. This may suggest an impure kaolinite or montmorillonite that is not captured in the cation sub-composition due to the relatively high sensitivity to K^+ in ~~our~~ the LAAPTOF measurement. A comparison of the sub-composition $(Al+Si)$ sub-composition with respect to alkali metals obtained by LAAPTOF $/(Al+Si+K+Na)$ obtained by SPMS and SEM measurement (Fig. 8) demonstrates a much greater sensitivity to alkali metals ~~than~~ in the SPMS measurement (due to low ionisation energy) than in the established filter technique. ~~Both~~ The SEM techniques show a qualitatively higher lower $(Al+Si)$ content in the Sahel $/(Al+Si+K+Na)$ ratio in the Moroccan sample (DDS01, panel (a)) compared to the Moroccan sample, Sahel sample (SDN02, panel (c)), but this is greatly exaggerated in the SPMS analysis (panels (b) and (d)) due selective ionisation of K and Na and the matrix effect.

In general, our analysis suggests the fine fraction of these North African soil samples to consist of *K* rich and *Al* rich clay minerals. This agrees somewhat with a comprehensive study of soil samples using many techniques by Engelbrecht et al. (2016) that concluded suspended mineral dust particle were primarily made up of two types of mineral assemblages; i) fragments of micas, clays, oxides, and ions of potassium (K^+), calcium (Ca^+), and sodium (Na^+) rich colloids in amorphous clay-like material, and ii) kaolinite with individual oxide mineral grains. The exception is that our measurements indicate that the potassium and sodium are retained in a 2:1 clay structure rather than in amorphous clay.

In order to explore the ~~amorphous and felsic composition~~ composition of potentially amorphous and feldspar matrix, we extracted particles with τ values of 0.58 - 0.8 into separate plots (Fig. 9). Perhaps unsurprisingly, the composition of these types of particles reflects the composition of clay particles (Fig. 4), with samples from the Sahel showing a greater loss of alkali metals due to weathering and diagenesis. It is not possible to separate felsic and amorphous material with any confidence, but it is reasonable to say that any feldspars that may be present in the Moroccan samples are fresher (un-altered) than their counterparts from the Sahel ~~due to the higher potassium content. It is known that K-feldspar is progressively altered to quartz and kaolinite if the potassium is removed by dissolution in the soil over .~~

The sample that has potentially the most feldspar grains is DDS01 which shows a small number of particles with a felsic composition in the SEM EDX analysis (Fig. 5(b)), and maybe a reflection of the river sediment containing freshly eroded rock from the Anti-Atlas mountain range. This sample also displays a distinct mode in the SPMS τ histogram in the felsic/amorphous region (Fig. 4(d)). In general, the SPMS crystal structure analysis in the τ histograms agree with the SEM EDX analysis of the distribution of composition in the samples. For example, the τ histogram of DDS02 indicates a predominately illite composition which is also reported in the narrow composition distribution in the SEM EDX analysis.

20 3.1.2 Internal mixing state of suspended natural soil

~~We approached the SPMS mixing state analysis using a similar method described by Sullivan et al. (2007b) where the relative signal of the chlorine (Cl^-) anion, ammonium (NH_4^+), and sulphate markers (SO_4^-) were considered, except we use the Org-Bio markers (CN^- and CNO^-) instead of ammonium to avoid comparing positive and negative ion peak areas. In addition to being a potentially important compound in changing the physiochemical properties of dust particles, chlorine has a high electron affinity and therefore Cl^- is a good reference signal, similar to the role of K^+ in positive ion mode.~~

Unlike the mineralogical composition, the mixing state of the natural soil samples varies quite a lot within the same PSA (Fig. 10). All samples contain particles with significant amounts of chlorine. Sample DDS03, collected close to a salt/silt plain, shows a relatively high sulfate content, probably associated with evaporite deposits.

The biggest difference however is the relative amount of org-bio internally mixed in the particles. This is further demonstrated in the histograms of the normalised org-bio content displayed in Fig. 11. Most samples contain particles with significantly less org-bio than chlorine, but samples DDS01 and SDN02, collected from a dry river bed and agricultural land respectively, have a number of particles where the org-bio signal is even stronger than that of chlorine, which is significant given the high electron affinity of the later.

3.2 The composition and transport history of transported dust (ICE-D)

In order to examine the properties of the transported dust in the ambient measurement, the mass spectra of silicate particles must be extracted from the general aerosol population. This was achieved using the fuzzy c-means clustering supplied with the data analysis software (LAAPTOF Data Analysis v1.0.2). The analysis was performed on positive and negative ion spectra and on negative ion spectra only. In both cases, silicate and calcium classes of particles were reported along with sulphate, carbonaceous and abundant sea-salt particles. Analysis using only negative ion spectra proved more useful in the evaluation of mixing state because it was not subject to false class divisions ~~because of peaks~~ caused by greater peak position shifting in positive ion spectra. A full description of the clustering analysis, including mass spectra of the cluster centers, is provided in supplement ~~S2 and~~ S3.

10 Averaged detection rate of the silicate and calcium particle types, as determined by the fuzzy clustering analysis, is displayed in Fig.12(a) with a 1 hour resolution . A previous comparison with an aerodynamic particle sizer indicated that the silicate particle count represented approximately 1% of the actual silicate present due to instrument function (Marsden et al., 2016). Nevertheless, the temporal evolution of the particle classes is representative and compares well to the the dust fraction of incandescent particles identified in tandem Soot photometer (SP2) measurement (Liu et al., 2018).

15 3.2.1 Calcium rich particles

Calcium carbonate ($CaCO_3$) is the most abundant non-silicate material in arid soils and is expected to be a major constituent in mineral dust aerosol. However, pure calcium carbonate particles were not observed in this ambient measurement. Alkaline calcium carbonate particles are expected to readily react with acid gasses in atmosphere to form calcium salts. The reaction of calcium carbonate with nitric acid ~~to form hygroscopic $Ca(NO_3)_2$~~ has been offered as a mechanism to explain ~~deliquesced calcium particles on filters~~ $Ca(NO_3)_2$ on filters exposed to dusty environments (Krueger et al., 2004; Laskin et al., 2005; Matsuki et al., 2005) collected after transport through urban and industrial areas. More recently, it has been suggested that in remote marine environments, a prevalence of HCl over HNO_3 would favor the formation of $CaCl_2$ as the principal calcium salt (~~Tobo et al., 2010; Kim and Park, 2012~~)

25 A distinct calcium chloride particle class is reported in this ambient measurement. These particles are characterised by signals of Ca^+ (m/z 40), CaO^+ (m/z 56) and $CaCl^+$ (m/z 75, 77) in positive ion spectra and Cl^- (m/z - 35, -37), and $CaCl_3^-$ (m/z 145, 147, 149) in negative ion spectra (See supplement S3.2). The temporal evolution of this particle class is similar to that of the silicate particle class (Fig. 12(a)), but very different to that of the sea-spray particles (see supplement S3.5), therefore we conclude that is has a similar source to the silicate and probably represents calcium carbonate that has been processed in the atmosphere .

30 3.2.2 Temporal evolution of the silicate particle mineralogy (ICE-D)

~~In a previous study using TEM of sliced dust particles collected in Tenerife, the majority of particles of transported Saharan dust were clay rich agglomerates composed of a ISCM matrix with inclusion of kaolinite and hematite (Jeong et al., 2016).~~

~~In light of this order to create a concise time series of the single particle mineralogy for the entire time period, the silicate class of particles in our ambient study is analysed making the assumption that each mass spectra in the ISCM category are representative of the average clay matrix in single particles.~~

5 ~~The silicate class of particles is differentiated into (previously identified by cluster analysis) was differentiated into a simple binary system of ISCM and non-ISCM by using the crystal structure analysis (τ parameter) to produce an time series of ISCM ratio (Fig. 12(b)). The ISCM ratio is the number of particles which have $\tau < 0.58$ divided by the number of silicate particles which have $\tau > 0.58$, representing ISCM and non-ISCM (feldspar, amorphous and very pure kaolinite) respectively. The start of the measurement period is characterized by relatively high ISCM ratio which is generally >1 . These conditions persist up until 17th August when the ISCM ratio is much lower than in the previous period with (ISCM ratio <1).~~

10 ~~The ISCM ratio and the (See section 2.1.1). The average detection rate of silicate and calcium containing particles are were combined to produce an hourly average of the ISCM, non-ISCM and calcium number fractions in mineral dust (Fig. 12(c)). It is noted Note that these fractions are relative to the detection efficiency of the instrument to each particle type, but the temporal evolution is representative. This display shows that an increase in calcium containing particles also occurs alongside the decrease in ISCM ratio on~~

15 ~~Most of the measurement period was characterized by relatively high ISCM ratio which is generally >1 . This is consistent with continuous long term off-line measurements of elemental composition around Cabo Verde by Patey et al. (2015) who concluded that illite was the most abundant clay mineral type. However, these conditions changed 17th August.~~

20 ~~We use August when the ISCM ratio is much lower than in the previous period with (ISCM ratio <1) and the fraction of calcium containing particle increases. We used the time series to define two dust events ; (D1 centered on 00:00 11/08/2015 and D2 centered on 15:00 17/08/2018. Sub-compositional analysis of the two dust periods 2018) which were analysed in more detail with sub-compositional analysis, using the same method as re-suspended dust, is displayed in Fig. 13. Dust applied to the soil dust samples.~~

25 ~~Silicate dust in event D1 has a composition that is relatively rich in illite contained a high fraction of ISCM type mineral composition with 2:1 phyllosilicate structure (blue circles in Fig. 13(a)), that plot close to the illite composition in the ternary diagram, similar to that observed in Moroccan soil DDS01 and DDS02 (Fig. 4(b, c)). This illite fraction, In contrast, these ISCM particles is much reduced in dust event D2 which has a higher proportion of non-ISCM felsic/felsic or amorphous material (red circles in Fig. 13(e)), and a shift away from the illite composition on the diagram. The actual mineral phase of these particles is less clear, but from the large fraction of these particle types and there central position on the ternary diagram it would be reasonable to assume an mixed amorphous matrix. It is clear however that the large fraction of particles with illite matrix present in D1 are absent in D2. The potential source and transport history of these material in these dust events is discussed in more detail after consideratin of the mixing state below.~~

3.3 Temporal evolution of the mixing state of silicate particles ~~The internal mixing of silicate dust is represented by (ICE-D)~~

The mixing of silicate and non-silicate within single particles may result from processes within the native soil (primary), or during atmospheric transport (secondary). The analysis of the suspended soil dust (INUIT09) shows mineral particles in North African soils are already mixed, particularly with varying quantities of chlorine, sulphate and organic/biological material. The internal mixing state of transported silicate dust (ICE-D) is reported with the sub-composition of markers of non-silicates in similar manner Chlorine - Org-bio - Nitrate, similar to the treatment of suspended dust in section ??except we consider, except we target nitrate in ambient particles instead instead of sulphate. Increases in nitrate have of sulphate because nitrate was present in low quantities in suspended soil. An increase in nitrate aerosol has previously been observed in association with air masses passing through Europe and Africa to Cabo Verde (Fomba et al., 2014), so this may be a useful indicator of the history of transported dust.

Nitrate In transported dust, nitrate mixing with the silicate dust is was varied, with the sub-composition of nitrate markers indicating a relatively greater quantity of nitrate mixing with silicate particles during the inter-dust period between the defined dust events. This shows showed a similar trend to the number concentration of nitrate sea-spray aerosol particle types extracted by fuzzy clustering (Supplement S3.5), which suggest the particles may have co-existed in the same air mass air mass for some period of time. There was a distinct drop in nitrate sub-composition during the dust period D2 when the crystal structure analysis suggests we also report a change in silicate mineralogy.

Internal mixing with organic-biological material was much less varied. Although it is not possible to conclude a primary or secondary processing source of organic/biological mixing, we observed less variation in mixing state in the transported dust than in the laboratory generated reference material. The number of particles that contain a significant fraction of this whose mixing state sub-composition contained more than 20% organic-biological material (Org-Bio > 0.2) varies with the dust concentration (Fig. 12(d)), and the median amount of organic-biological marker signal is fairly stable, with the exception of a 24 hour period following dust event D1 (Fig. 12(e)). This may be informative of how well mixed local sources of dust become after emission, but could also be a reflection of atmospheric processing.

Particle mixing is important because the efficient ice nucleating properties of proteinaceous INP can be transferred to dust particles after mixing ((Augustin-Bauditz et al., 2016; O'Sullivan et al., 2016)). It is interesting to note that Price et al. (2018) did not see significant variation in INP concentration in aircraft based studies of the Saharan air layer during ICE-D, despite geographically widespread sources of that dust. The origin of the organic-biological markers CN^- and CNO^- in these dust particle requires further investigation. Zawadowicz et al. (2017) demonstrated a method of distinguishing between biogenic and in-organic ion signals using a different SPMS instrument (PALMS), but it is not yet proven to be transferable to other instruments designs.

3.4 Potential source areas and transport history

Dust transport to Cabo Verde is controlled by the position of the Azores high pressure system whose anticyclonic flow results in persistent north easterly trade winds along the coast of Morocco, Western Sahara and Mauritania (Carpenter et al., 2010). Dust concentrations at ground level are influenced by the dust deposition rate which is strongly dependent on the horizontal and vertical dust distribution (Schepanski et al., 2009a). During the summer months, the westward moving SAL typically occurs

at relatively high altitudes (1-6km) in the Cabo Verde area (Tsamalis et al., 2013), and the warm, dry, dust-laden air creates a stable layer that is separated from the lower levels by a strong temperature inversion (Wong et al., 2009). We used back trajectory analysis, satellite observations and our measurement of dust mineralogy and mixing state to give potential source areas and transport history of two dust event observed at Cape Verde in the summer of 2015.

5 Back trajectory analysis of ~~the dust events~~ both dust events (D1 and D2, defined in the analysis above), shows transport in the trade winds within the marine boundary (Fig. 13c, g). ~~The influence of air mass~~ Influence from the African continent is evident during D1 ~~and the high ISCM ratios for in these silicates (68%) suggests this material originated from the Northern region of the Sahara. The back trajectories indicate that when~~ some of this air mass was lofted over the Atlas Mountains, Morocco before descending into the ~~MBL~~ marine boundary layer (MBL). The high ISCM ratio we measure (68%) is consistent with ~~Scheuvens et al. (2013) who suggested illite/kaolinite ratio >2 are indicative of the PSA that comprises the northern part of the west coast of Africa and the south eastern slopes of the Atlas Mountains. Dust mobilisation associated with density currents related to moist convection has been observed on the Sahara side of the Atlas Mountain chain (Knippertz et al., 2007).~~ Satellite observations ~~show at the time showed~~ a plume of dust developing in Algeria and crossing the Atlas mountains and then above the Atlantic Ocean in the days preceding the dust event D1 (Supplement S5). However, source activation observed ~~by remote satellite is subject to errors associated with the temporal resolution of the measurement (Schepanski et al., 2012). Dust emission associated with density currents related to moist convection has been observed on the Sahara side of the Atlas Mountain chain (Knippertz et al., 2007), where the soil mineralogy is close match to the material we report in this dust event. The Anti-atlas mountains was also suggested as a source of micronutrients in sediment traps in the North East Atlantic Ocean by Chavagnac et al. (2007).~~

20 A feature of these back trajectories is that the air mass arriving during ~~In contrast, back trajectories for D2 suggest this air mass was never lofted over Africa, but~~ came into direct contact with the coastline of Mauritania ~~which~~. This is a possible source of dust. ~~This that~~ could explain the relatively low ISCM content and relatively high calcium carbonate fraction which is consistent with source sediments of the Atlantic Coastal basin (Moreno et al., 2006). ~~The particle size distribution of the silicate from D2 also suggests that this dust may have been transported a relatively short distance compared to D1 (Fig. ??). The silicate from D1 has a well-defined mode at approximately 1µm, which is in contrast to the broader distribution of D2 particle sizes, which extends above 2µm.~~ In off-line filters collected at Praia, Cabo Verde, Kandler et al. (2011b) reported illite/kaolinite ratio of between 1:2 and 1:4 during winter transport of dust from coastal Mauritania and Mali respectively.

The nitrate mixing state of particles also suggests different transport pathways for the two dust events. The mixing of nitrate with silicate during and after D1 indicates ~~heterogeneous reaction with nitric acid in polluted air~~ contact with polluted ~~air~~, and is consistent with transport from the North, as reported by Salvador et al. (2016), whilst the cleaner particles in D2 indicate that no such mixing took place. An increase in the fraction of sulphate containing sea-spray aerosol in D2 on the other hand (Supplement S3.5) may be associated with ~~biogenic sources from coastal upwelling~~ organosulfur containing compounds from biogenic sources in the coastal upwelling region off the coast of Mauritania. In addition, the particle size distribution of the silicate from D2 also suggests that this dust may have been transported a relatively short distance compared to D1 (See

supplement S4). The silicate from D1 has a well-defined mode at approximately $1\mu\text{m}$, which is in contrast to the broader distribution of D2 particle sizes, which extends above $2\mu\text{m}$.

4 Discussion

In this analysis, we assert that an approximation of the silicate mineralogy of the fine fraction can be made by considering the dust particles as clay mineral matrices with additional felsic/amorphous grains. We focus on the relative abundance the K, Na and the combined Al and Si signals, all of which are readily observed in the mass spectra. Although a non-quantitative measurement, this provides a relative assessment of the interstitial cation content relative to the tetrahedral and octohedral co-ordinated cations, which together define mineral phase. This makes the assumption that Mg, Fe and Ca are of minor importance in silicate mineralogy in continental sediment. While certainly untrue at a local level, it is informative of the genesis and subsequent weathering history of the clay fraction in soil on a continental scale.

The ability of SPMS to report crystal structure enables the differentiation of clay minerals from felsic/amorphous material, which can then be analysed separately using sub-composition analysis. Although non-quantitative, the sensitivity of the SPMS technique to potassium and sodium makes it particularly suitable for differentiating kaolinite from illite in the fine fraction, but is less effective than SEM-EDX at identifying silicate particles rich in magnesium and calcium due to suppression by the matrix effect and interference from poorly resolved peaks. However, the division of clay species is also difficult in off-line analysis and kaolinite and illite are often the only clays species detected by XRD in aircraft studies (Formenti et al., 2014), therefore these types of on-line measurements are likely to be of some use in the study of mineral dust.

Sub-compositional analysis is a techniques that is commonly used for the analysis of complex chemical relationships in circumstances in which the full composition of a substance is impossible to obtain, such as in whole-rock geochemical analysis, where it is convenient to describe the composition in terms of a relative measurement of carefully chosen components. The ternary diagram provides an intuitive way of displaying relative information whilst avoiding some of the sub-compositional incoherence associated with two component systems. With due respect to the matrix effect in SPMS, these diagrams can be used to provide mineralogy and mixing state of natural dust relative to laboratory generated standards.

Using sub-compositional analysis, a distinct illite rich composition is observed in the Moroccan samples compared to a kaolinite rich composition in samples from the Sahel region. The crystal structure analysis confirms a 2:1 phyllosilicate structure for particles with illite composition but also suggests a 2:1 structure in many particles with a Kaolinite composition, which may represent an impure kaolinite compared to the CMS standard (KGa-1b). Minerals undergo significant alteration and weathering in the soil making pure minerals difficult to identify, even by XRD of the bulk sample (Formenti et al., 2014). Nevertheless, the fraction of illite and non-illite particles is a useful indicator of PSA, similar to the illite/kaolinite ratio. Many more SPMS measurements are required to fully understand the clay ratio signatures at source and how this is maintained after varying distances of transport and mixing.

It was suggested by Scheuvens et al. (2013) that illite/kaolinite ratio >2 are indicative of the PSA that comprises the northern part of the west coast of Africa and the south eastern slopes of the Atlas Mountains. The Anti-atlas mountains was also

suggested as a source of micronutrients to the North-East Atlantic Ocean by Chavagnac et al. (2007). In off-line filters collected at Praia-Cabo Verde, Kandler et al. (2011b) reported illite/kaolinite ratio of between 1:2 and 1:4 during winter transport of dust to Cabo Verde from coastal Mauritania and Mali respectively. In continuous long term measurements of elemental composition, Patey et al. (2015) reported seasonal variation in Al content which was attributed to seasonal changes in dust transport, and reported illite as the most abundant. In this later case, only a limited number of filter samples were selected for XRD analysis and the reported clay mineral fractions were subject to large errors due to low sample loading and preferred orientation of the grains. In all the above off-line studies, filters were exposed for around 1 day resulting in poor temporal resolution of the data. Our high resolution measurements show that the mineralogy and mixing site of dust can change on a hourly basis, suggesting that changes in dust source, transport pathways and particle composition may be lost in off-line data.

The mechanism by which dust enters the marine boundary layer (MBL) is crucial to understanding its source and transport history in ground based measurements. Dry deposition of mineral dust from a lofted Saharan air layer (SAL) by gravitational settling is expected to be a slow process for particles of this size, although dust entrainment by convective processes may bring larger quantities of material from the free troposphere (Bravo-Aranda et al., 2015). The deposition rate of particles is an active topic of research with recent work suggesting a coarse mode is maintained longer than expected (several days) by atmospheric dynamics ((Denjean et al., 2015; Weinzierl et al., 2017)).

In a For example, in XRD analysis of material captured in marine sediment traps of Cape Blanc, Mauritania, Friese et al. (2017) concluded that seasonal variation in mineralogy occurred due to changes in transport pathways; from long-distance transport in the SAL during summertime, to local transport in the trade winds in winter. Our measurements also suggest two pathways for dust arriving at Cabo Verde, but with a much finer temporal resolution. We propose that in August 2015, illite rich dust from the NW margin of the Sahara was advected into the free troposphere and became mixed in to the MBL off the coast of Morocco before several days transport to Cabo Verde. An eastward shift in the Azores high results in the direct entrainment of dust into the MBL from the coast of Mauritania, producing a relatively illite poor and calcium rich dust event in Cabo Verde on 17th August that lasted for several hours. This is supported by the nitrate content which is high in the dust transported from the North of Cabo Verde, as demonstrated by Salvador et al. (2016) a few hours. In all the above off-line studies, filters were exposed for around 1 day resulting in insufficient temporal resolution of the data.

One of the more surprising results of this work is the relatively small variation in the organic-biological mixing in comparison to the laboratory generated reference material. This is in spite of differences in source and transported history apparent in the mineralogical analysis. This may be due to a greater chlorine content that perturbs our relative measurements, but it is interesting to note that Price et al. (2018) did not see significant variation in ice nucleating particle (INP) concentration in the accompanying aircraft sorties despite geographically widespread dust sources. This is important because the efficient ice nucleating properties of proteinaceous INP can be transferred to dust particles after mixing ((Augustin-Bauditz et al., 2016; O'Sullivan et al., 2017). The origin of the organic-biological markers CN^- and CNO^- in these dust particle requires further investigation. Zawadowicz et al. (2017) a method of distinguishing between biogenic and inorganic signals using a different SPMS instrument (PALMS)

4 Conclusions

We present a detailed characterization of the mineralogy and mixing state of the fine fraction ($< 2.5\mu\text{m}$) of North African mineral dust using a novel combination of sub-composition and crystal structure analysis with a single particle mass spectrometer. Despite the fact that the technique provides incomplete coverage in terms of particle number, elemental composition, and mineralogy; it was possible to clearly detect regional differences in the mineralogy in single particles of suspended soil and ambient transported dust.

These conclusions were made under the reasonable assumption that single particles in the fine fraction were composed of either clay minerals or feldspars/amorphous matrix, a distinction that can be realised by our novel crystal analysis technique. Although the SPMS technique is shown to be generally non-quantitative with respect to the elemental sub-composition of pure mineral phases such as illite and K-feldspar, a semi-quantitative (relative) measurement of elemental composition can be achieved after particles are separated into mineral groups based on crystal structure. Further differentiation of mineral phase can then be made by comparison to pure mineral fingerprints from within the mineral group. This indicates the importance of particle structure in addition to particle composition in the matrix effect in SPMS.

The sensitivity of the technique to potassium, sodium and aluminum makes it particularly useful for differentiating illite (potassium-rich clay), montmorillonite (sodium-rich clay) and kaolinite (aluminum-rich clay) clay mineral assemblages. Comparison with off-line SEM EDX analysis of the suspended soil confirms the observations of a composition close to illite is observed in Moroccan samples compared to a kaolinite composition in samples from the Sahel, in agreement with geology of these regions. SPMS is less effective than SEM EDX at identifying particles rich in magnesium and calcium due to suppression by the matrix effect and interference from poorly resolved peaks, but it is ~~not yet proven to be transferable to other instruments designs.~~

~~Using a combination of novel sub-composition and crystal structure analysis, we present a detailed characterization of the mineralogy and mixing state of the fine fraction ($< 2.5\mu\text{m}$) of North African mineral dust. Differences in clay mineralogy likely that these elements are derived from carbonates and oxides and are not strictly necessary to classify the silicate minerals. This makes the assumption that Mg, Fe and Ca are of minor importance in silicate mineralogy in continental sediment, which is certainly not true on a local level. However, our measurement show it is not necessary to include this when considering the genesis and subsequent weathering history of the clay fraction in soil on a continental scale are detectable, with Moroccan dust high in ISCM and Sahelian dust dominated by kaolinite like minerals.~~

These results show that the SPMS and SEM EDX techniques are complimentary, with SPMS providing a high resolution on-line indication of mineralogy and mixing state of the principal particle matrix, and SEM EDX providing semi-quantitative elemental composition of all particles, including material that the SPMS may not ablate. In most cases, both techniques show the distribution of mineralogical composition is more continuous than clustered in distinct mineral phases, and only laboratory suspended river sediment from the Anti-Atlas Mountains, Morocco contained a distinct mode of felsic particles in the fine fraction fine particles with a feldspar matrix.

The detailed analysis of laboratory suspended dust provided useful reference data for the interpretation of the origins and transport history of ambient dust in the remote North Atlantic. ~~Relatively~~ Although semi-quantitative in terms of particle

number fractions due to number counting bias effects associated with instrument function, the relative temporal trends are very informative. A relatively large numbers of illite rich particles (ISCM Ratio > 5) suggests a dust source on the NW margins of the Sahara during the summer, but the mixing state is key to understanding the transport history. Internally mixed nitrate suggests. However, a rapid change (< 1 hour) towards a felsic/amorphous particle matrix (ISCM Ratio < 1) was observed in silicate particles when back-trajectories suggest direct emission into the marine boundary layer from the West African coast. This episode lasted only a few hours and challenges previous findings from off-line measurements that the source and composition of transported dust only change on a seasonal basis.

Internal mixing state was of some use to understanding transport history of ambient dust, but must be used with caution because some degree of mixing was already present in the primary soil. However, variations in internally mixed nitrate suggested dust from the NW margins of the Sahara was deposited into the marine boundary layer after transport in the Saharan air layer. In contrast, this nitrate mixing was much reduced during a short dust event, for which back-trajectories suggest direct emission into the marine boundary layer from the West African coast. The relative concentration of organic/biogenic biological markers did not vary significantly in transported dust, but had significant local variation in suspended soil samples, making them less useful for interpreting source and transport history. The transport pathways, but potentially informative of how well mixed local sources become after emission. The primary and secondary origin of these chemical markers and how they change the physiochemical properties of dust particles requires further investigation.

These results show that the SPMS and SEM-EDX techniques are complimentary, with SPMS providing a relative indication of mineralogy and mixing state of the principal particle matrix, and SEM-EDX providing semi-quantitative elemental composition of all particles, including material that the SPMS may not ablate. Although non-quantitative, the SPMS techniques are particularly sensitive to the potassium and sodium content of dust particles which makes them suitable for differentiating continental sediments in real time. These measurements show that changes in mineralogy of ambient aerosol particles can be detected with high temporal resolution using SPMS.

The combination of online on-line mineralogy and mixing state of ambient dust has potential for resolving the complexity of dust dust-emission, transport and deposition. These examples of aged transported dust should also be useful in obtaining atmospherically relevant test material for laboratory experiments of ice nucleation and radiative properties, but more high resolution measurements at varying distance from potential dust sources are required to fully understand the complexity of atmospheric dust transport these processes. The example of transported dust provided here should also be useful for studies of ice nucleation, radiative effects, and heterogeneous reactions involving mineral dust.

Data availability. LAAPTOF soil dust characterisation data collected for the INUIT09 campaign at the AIDA facility is available at <https://data.eurochamp.org/data-access>. Data collected during the ICE-D campaign are available from the British Atmospheric Data Centre, Centre for Environmental Data Analysis (2018, <http://www.ceda.ac.uk/>), at the following URL: <http://catalogue.ceda.ac.uk/uuid/d7e02c75191a4515a28a20> (Bennett, 2018).

Author contributions. The document was principally written by N.Marsden with input from R.Ullrich and S.Eriksen Hammer. The INUIT09 project was devised and managed by R.Ullrich and O. Möhler, with SPMS data acquired by N.Marsden. The ICE-D field data was acquired by N.Marsden and P.Williams with support from M. Flynn, J.Allan and H.Coe. Data processing was performed by N.Marsden (SPMS) and S.Eriksen Hammer (ESEM) with support from K.Kandler. Back trajectory analysis by D.Liu and Z.Cui

5 *Competing interests.* No competing interests declared.

Disclaimer. TEXT

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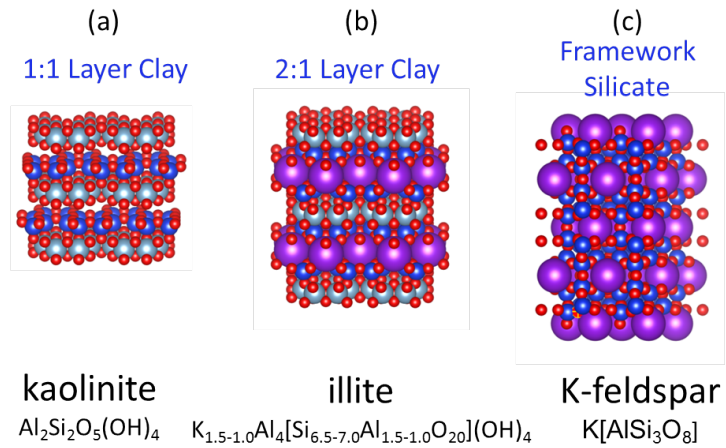


Figure 1. The crystal structures of common aluminosilicate minerals (a) 1:1 clay mineral structure of kaolinite, (b) the 2:1 clay mineral structure of illite and (c) the framework structure of k-feldspar. Color code is as follows; Red = anions (O, OH), Grey = octahedral co-ordination (Al, Mg), Blue = tetrahedral co-ordination (Si, Al), purple = interstitial complex (K, Na, Ca).

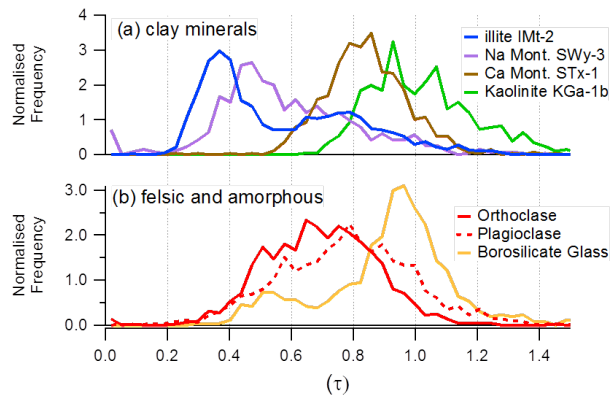


Figure 2. Histograms—The differentiation of the reference minerals using crystal structure analysis described by Marsden et al. (2018). The peak shift ratio ratios (τ) for were calculated from ion arrival times from individual particles in the mass spectrometer, rather than conventional peak area analysis for elemental composition. Nominally pure mineral dust was sampled after dispersed in a dust tower. (a) nominally pure clay minerals from the clay mineral society and (b) feldspars (orthoclase and (K feldspar), plagioclase (Na feldspar) and borosilicate glass.

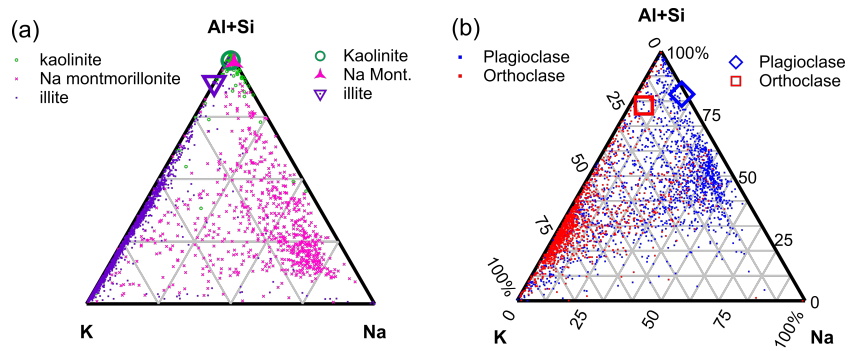


Figure 3. Ternary plots—The differentiation of the Al+Si, K and Na content in single particles from lab-generated reference material/minerals using sub-compositional analysis. Each dot in the ternary plots represents the composition of a single particle whereas larger icons represent bulk composition by XRF analysis. Nominally pure mineral dust was sampled after dispersed in a dust tower (a) Nominally-nominally pure kaolinite/clay minerals illite (1806), Na-montmorillonite-kaolinite (1388 particles) and illite-Na-montmorillonite (800 particles) from the clay mineral society (CMS sample ID KGa-1b, SWy-3 and IMt-3 respectively) (b) orthoclase (K feldspar crushed from large crystals, 1318 particles) and plagioclase (Na feldspar, 1568 particles).

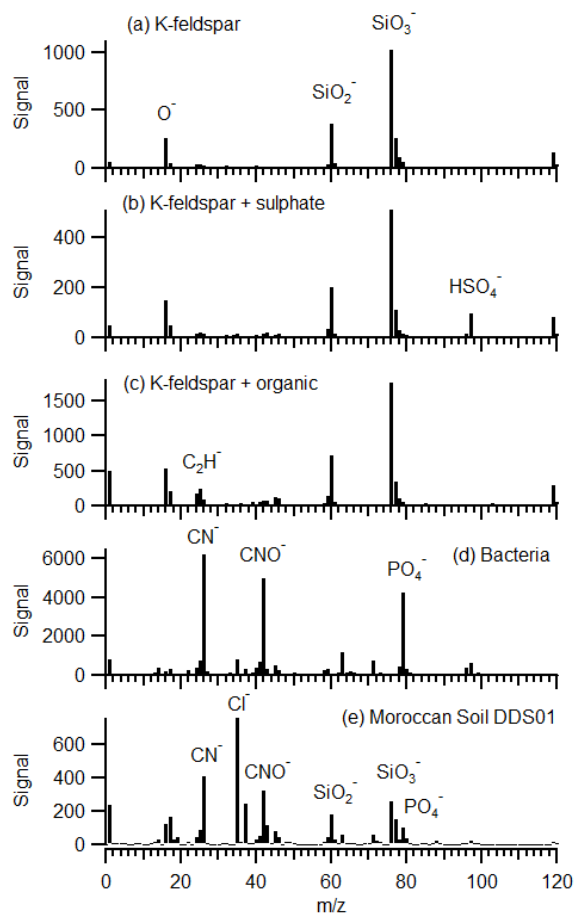


Figure 4. Average negative ion mass spectra (200 particles) of re-suspended material in the AIDA chamber during the FIN-1 campaign. (a) pure K-feldspar, (b) K-feldspar with sulfate coating, (c) K-feldspar with organic coating, (d) bacteria and (e) Moroccan soil dust DDS01 during INUIT09.

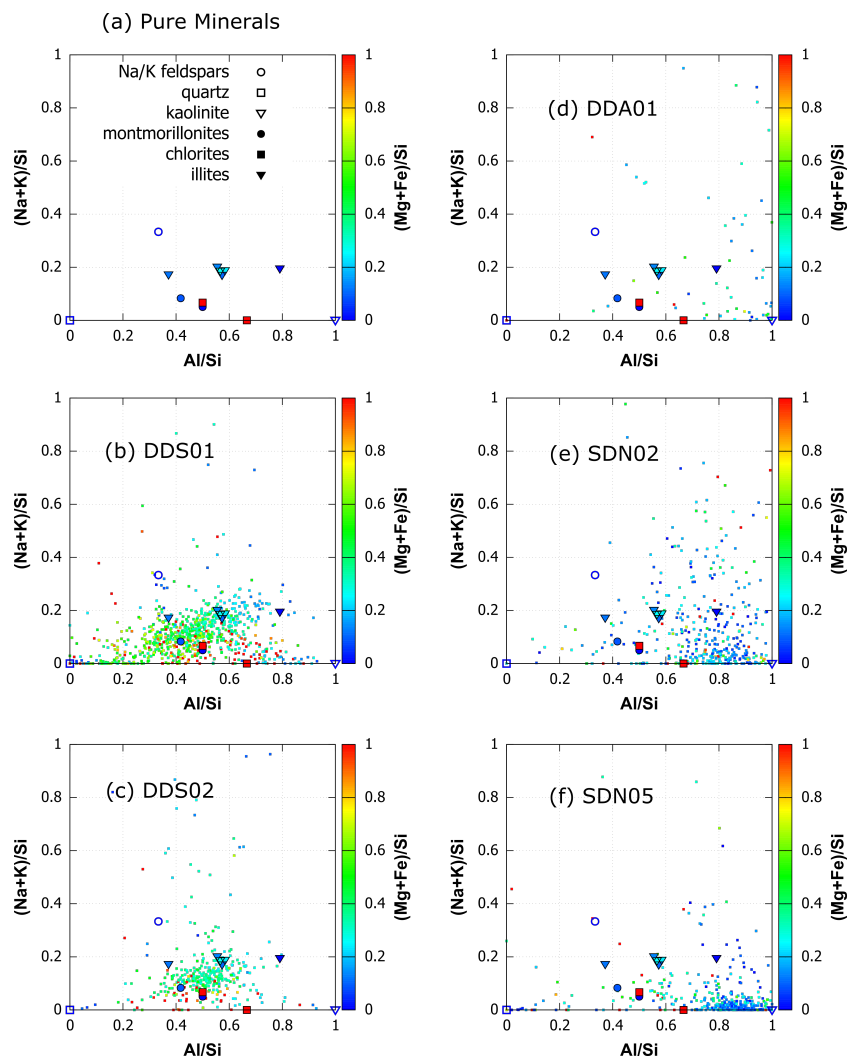


Figure 5. Elemental sub-composition diagrams of suspended natural soil samples (INUIT09) by SEM EDX analysis. (a) average composition of nominally pure mineral samples, (b) DDS01, (c) DDS02, (d) DDA01, (e) SDN02, (f) SDN05. Ratios are calculated from atomic %

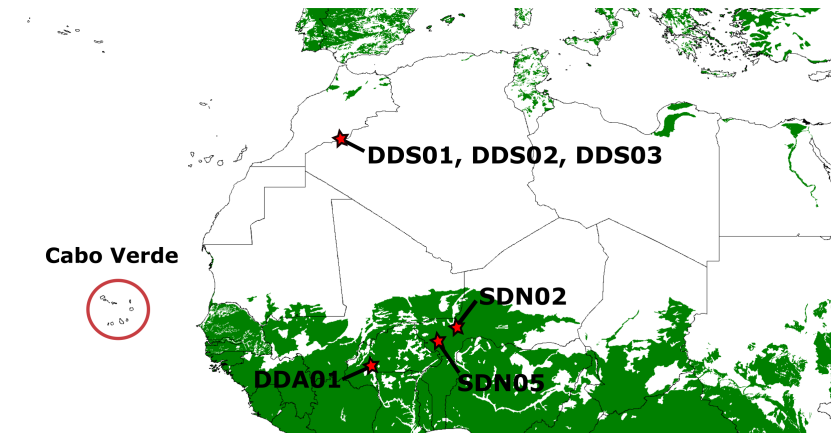


Figure 6. Sampling locations of natural soil (stars) and transported dust at Cabo Verde (circle). The green color indicates soils that have a cation ion exchange capacity (CEC) of less than 35 cmol/kg indicating kaolinite rich soil. Produced from the Digital Soil Map of the World.

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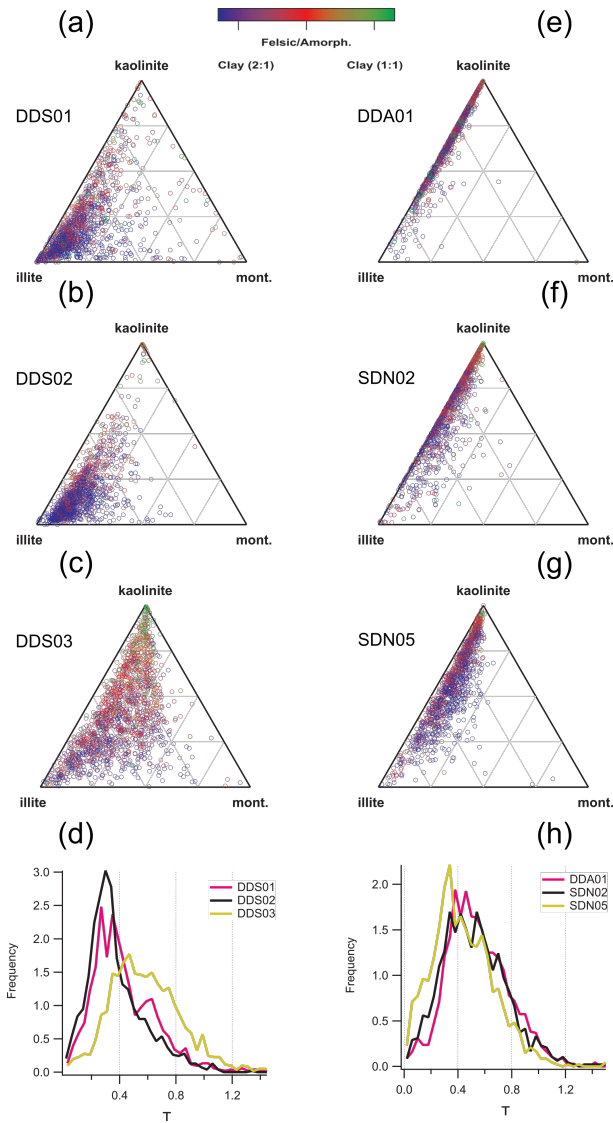
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Ternary plots referenced to the inferred kaolinite, illite, Na-montmorillonite end members of the clay mineral series using the Al+Si, K, and Na content of lab-suspended natural soil samples ratios from reference minerals (Fig. 3). Samples from Morocco in the left column (a, b, c), and samples from the Sahel in the right column (e, f, g). The color function is proportional to the τ parameter of as defined by the crystal structure which analysis technique, so that the blue dots represent 2:1 clay minerals. The distribution of τ for each sample is also displayed as a histogram (d, h). Each plot contains (2000 particles analysed in each sample)

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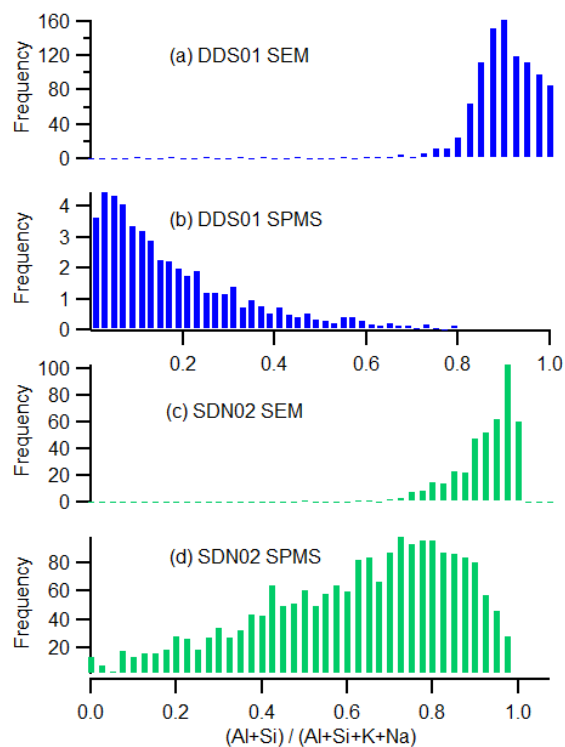


Figure 8. A comparison of the relative sensitivity of the SPMS and SEM techniques to the principal elements in silicate minerals. Histograms represent the sensitivity to alkali metals of the Al+Si sub-composition interstitial complex with respect to alkali metals the Al and Si of the silicate structure $((Al+Si)/(Al+Si+K+Na))$ in single particles of Moroccan soil sample DDS01 (a, b) and compared to Sahelian soil sample SDN02 (c, d) samples using the SEM and SPMS technique respectively.

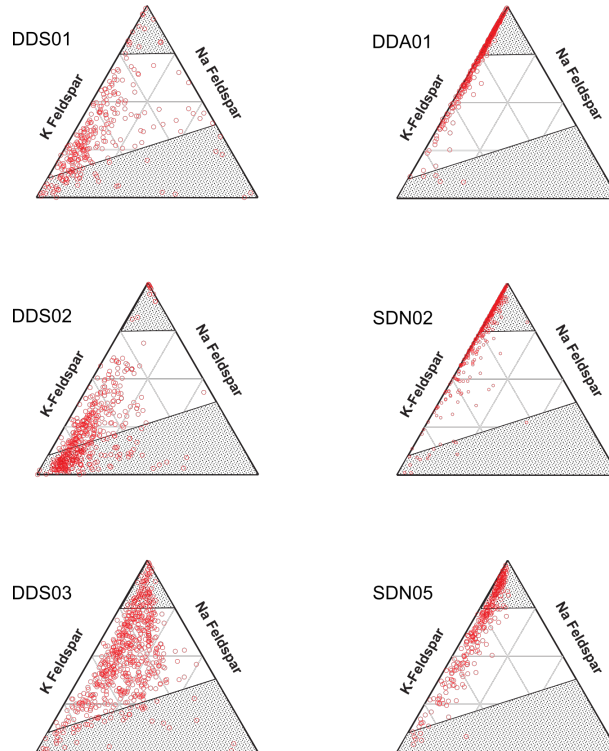


Figure 9. Ternary-plots Sub-compositional analysis of the Al+Si, K and Na feldspar/amorphous content of the in suspended natural soil samples (INUIT09) by SPMS. The felsic/amorphous fraction as determined was selected by crystal structure analysis ($\tau = 0.58 - 0.8$) in lab-suspended natural soil samples from Morocco (a, b, c). The ternary diagrams are referenced to the inferred K and Na end members of the Sahel (d) feldspar series using the Al+Si, eK, f and Na ratios from reference minerals (Fig. 3). The greyed out area represent unlikely composition of feldspar as demonstrated by the fingerprint in Fig reference minerals. 3. Samples from Morocco in the left column (a, b, c), and samples from the Sahel in the right column (e, f, g)

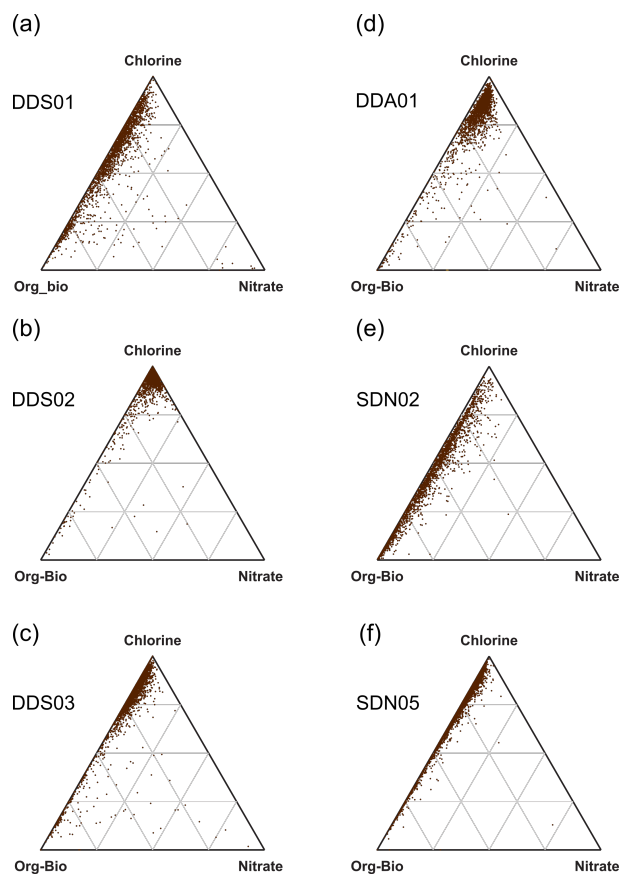


Figure 10. Sub-compositional analysis of the non-silicate content in suspended natural soil samples (INUIT09) by SPMS. Ternary plots of the Cl, organic-biological and sulphate marker peak areas in Moroccan (a, b, c) and Sahelian (c, d, e) re-suspended soil dust. (2000 particles analysed in each sample)

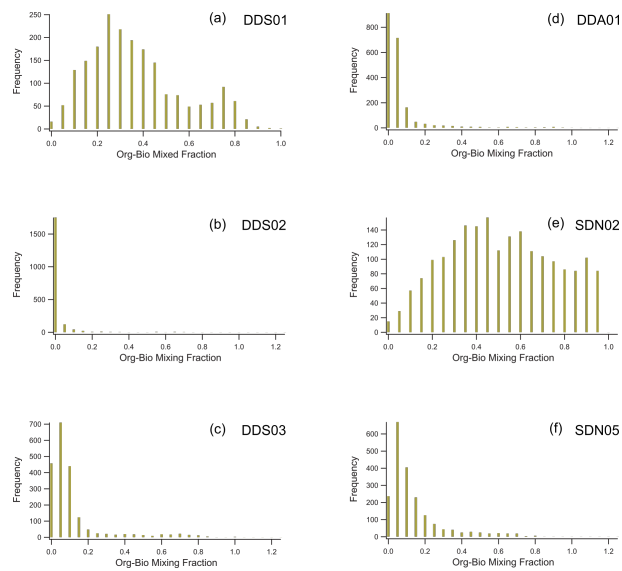


Figure 11. A comparison of the relative organic/biological content in the non-silicate portion in suspended natural soil samples (INUIT09). Histograms are of the normalised Org-Bio sub-composition from fraction in single partiele-particles of Moroccan (a, b, c) and Sahelian (d, e, f) samples.

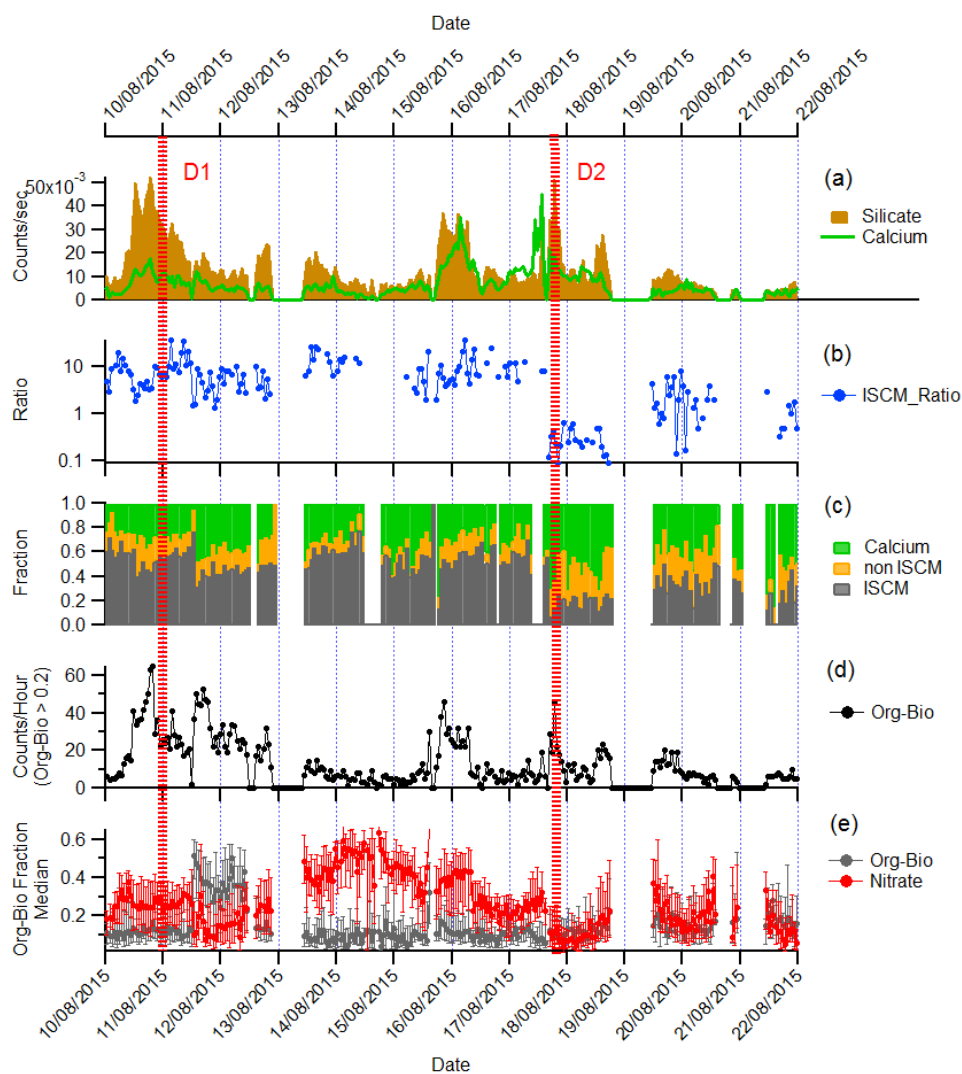


Figure 12. Time series (1 hour resolution) of ambient dust properties measured at Cabo Verde during the ICE-D campaign by LAAPTOF SPMS. [A total of 12698](#) (a) concentration of silicate and calcium rich particles ([total measurement of 12698 silicate and 6837 calcium rich particles](#)). (b) Hourly average ratio of ISCM to non-ISCM minerals ([ISCM Ratio](#)) determined by crystal structure, (c) Hourly particle number fraction of calcium, ISCM and non-ISCM particles. (d) Hourly concentration of silicate particles with organic-biological sub-composition > 0.2. (e) Hourly median Org-Bio and nitrate sub-composition marker quantity. Error bar is 25th and 75th percentile.

Vacuum aerodynamic size distributions of silicate particles in dust event D1 and D2.

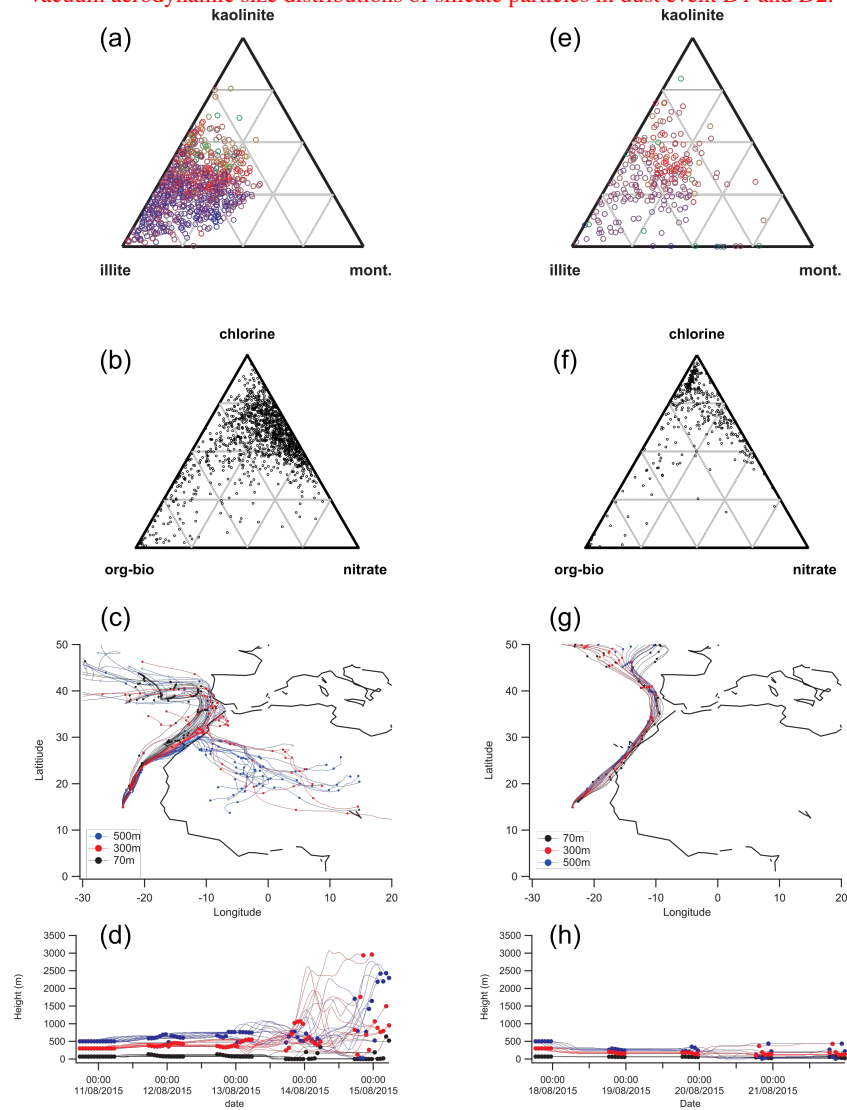


Figure 13. Sub-composition Analysis of the mineralogy and transport history-mixing state of dust events D1 in the left column (a-d) (1301 dust particle analysed) and D2 in the right column (e-f), showing mineralogy (378 particles analysed). Mineralogical analysis by SPMS shows the high number of illite particles (blue circles) present in D1 (a and d) are absent in D2 (e). In addition, mixing state analysis shows a higher proportion of particles mixed with nitrate in D1 (d and h) than in D2 (f and h) and. HYSPLIT back trajectory analysis suggest influence of air masses from the Sahara during D1 (c, d,) and coastal Mauritania during D2 (g, h).