Interactive comment on "Mineralogy and mixing state of North African mineral dust by on-linesingle-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 atmosphericprocessing 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 assignements.

Page 15, line 10: "Sub-compositional analysis is a techniques" – should be technique.
Corrected!