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Atmospheric Chemistry and Physics
Discussions

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.

Anonymous Referee #1

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Marsden et al. use laser desorption/ionization single-particle mass spectrometry to analyze source mineral dust particles, and ambient dust-laden aerosol sampled in North Africa. They apply their recently developed mass spectral analysis method to distinguish between different silicate minerals, based on the time delay that the relevant ions are detected in the MS. This time delay relates to the crystal structure of the different mineral phases. Distinguishing between different specific mineral phases or families in individual particles is a serious analytical challenge. The results presented here are quite novel, despite the various issues related to the semi-quantitative nature of the analysis, only being able to identify or distinguish some of the major mineral phases, and not achieving complete separation between different phases (the spread in the delay time for different "pure" minerals is quite large with significant overlap). 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 between distinguishing between mineral phases.

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.

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 sub0section 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.

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

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).

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)

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).

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.

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.

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?

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.

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).

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

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

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?

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.

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.

7/7: Reactions with ozone will just convert O_3 to O_2 on dust, and not add any material.

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.

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).

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.

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)

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.

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

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.

Sect. 3: Again odd to just have one sentence, and this one has many syntax errors/typos.

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.

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

11/12: felsic means felspars?

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

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 actually particle hit percentage?

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?

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

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

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.

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

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

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

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

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

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.

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?

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.

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.

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.

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

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

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

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

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-.

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.

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

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

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

Pg 2/line 21: “affects” not effects.

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