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 #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 between 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 a.l, 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{Hinz2006, 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,DallOsto2010,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{Christopoulous2018}, 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 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 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)

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 $Al^{+}+Si^{+}, K^{+}, Na^{+}$, cations readily observed in the SPMS of mineral dust (m/z 27, 28, 39, 23 respectively), using the assumption that the fine fraction ($<2.5\mu m$) 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 O_3 to O_2 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, C_2^+ could also come from black carbon that was mixed with the particle. I would be wary of using C_2^+ 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 in-organic 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 is 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 to 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 felspars?

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-Altas 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 actually 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 Altantic"

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 be 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 tranported 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 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