

Reply to Referee # 1

Authors' Response (AR) in blue

General assessment

This ms. characterizes the mineralogy and chemistry of the Saharan dust deposited in Granada, Spain, in one extreme dust event. It also investigates the trajectory of the winds carrying the dust and the dust sources. These results are compared with abundant literature of Saharan dust transport, mineralogy and chemistry. All the above is a very complete study carried out with competence and thoroughness. Beyond this, the ms includes a lengthy discussion on three broad issues: Fe bioavailability in Saharan dust, effect of Saharan atmospheric dust on radiative forcing and effect on human health. These discussions are kept at a general, non-specific level and are given a relevance which is not warranted either by the data provided in the ms or the depth of the discussion. After all, the ms provides data from one event only, and this and extreme event, rare by definition. The ms does not contribute data with sufficient perspective to allow the wide discussion on the above issues. In my opinion, this discussion needs to be re-written in a focused way, more closely linked to the ms results and, if possible, using a quantitative approach that illustrates the magnitude of the relevance of the results. Such amended version of the ms would be within the scope of ACP. If the discussions on Fe bioavailability, effect on radiative forcing and effect on human health were removed the ms would have a much smaller scope, consisting on the detailed characterization of an extreme dust event.

The text can be condensed. Some ideas are repeated several times in the ms.

Authors' response (AR): We thank the referee for the thorough review of our Ms and for his overall positive opinion about the completeness of our study. We also thank him for underlining the competence and thoroughness of our work. We appreciate his comments regarding the need for a more focused discussion. In the revised version of the manuscript, a more focused discussion avoiding repetition and underlining the limitations of our results to draw too general conclusions is presented. Additionally, all the technical issues indicated by the referee have been addressed (see below). Note: unless specified, all references cited in this AR are included in reference list of the revised version of the Ms.

Major issues

Discussion of Fe bioavailability. A lot of this discussion reviews known facts and discusses them in a general way, without quantitative data. The significance of the results from the ms for Fe bioavailability is not sufficiently supported. In my opinion, the authors could try to assess the amount of bioavailable Fe in the investigated dust and compare it with quantitative results in the literature. They could also try to project the results to marine areas seeded by the Sahara, comparing with previous estimates. Even if these projections have large uncertainty, they will allow some assessment of whether the results in the ms suggest changes to our understanding of input of bioavailable Fe to the ocean from the Sahara.

AR. We feel that due to the importance of the topic and the broad audience of Atmospheric Chemistry and Physics, the review of facts regarding dust Fe bioavailability and impact is necessary to follow the results that we present and discuss in this section.

Following this referee's suggestion, in the revised version of the Ms. we include the results of the analysis of the bioavailable soluble Fe determined from standard leaching tests using both MilliQ water (pH 5.6) and an ammonium acetate buffer solution (pH 4.7). The protocol for such dissolution tests and analyses are now indicated in the Materials and Method section. We have discussed both our quantitative results on amorphous and/or poorly crystalline Fe content in the studied dust as well as our new soluble iron results in lieu of the existing literature. Based on this quantitative comparison with published results, we now emphasize that the amount of bioavailable Fe (from dissolution of -colloidal- amorphous or poorly crystalline ferrihydrite, as well as from dissolution of clays) already present in dust source areas may have been underestimated, particularly because in the case of the amorphous or poorly crystalline phase, it is difficult to identify and quantify. We also point out that the fractional iron solubility, FFS, of our samples is double than the value of amorphous/poorly crystalline Fe-oxihydroxides we have determined upon a careful reevaluation of our TEM-AEM results, as well as the quantitative XRD results (see answer to Referee #2). This is interpreted considering that the rest of soluble iron comes from dissolved structural iron (i.e., from the Fe-containing clay minerals). Finally, we quantitatively compare our FFS results with published ones for the Atlantic and Mediterranean areas.

The authors state that the amount of soluble Fe typically increasing during long-range transport, from ~1% up to 80%. The simplest mechanism to explain this is that the larger particles drop during transport, causing a concentration of smaller, more soluble particles. With this mechanism, the total amount of soluble Fe in dust does not increase with transported distance. Fe-solubility, as indicated by the authors (lines 7-10 on p. 31), is mainly a function of particle size.

AR. The idea of establishing a relationship between transport distance/time and preferential deposition of larger particles leading to an apparent increase in soluble iron, as originally proposed by Baker and Jickells (2006) (for the case of Saharan dust transported across the North Atlantic) has been discredited by subsequent studies. In a study by Shi et al (2011a), cited in the revised version of the Ms, where both Baker and Jickells are co-authors, it is clearly demonstrated that physical size sorting has a very minor (if any) effect on iron solubility: other effects such as atmospheric processing (including photo-oxidation and aerosol acid processing) and mixing with anthropogenic (Sholkovitz et al., 2009; 2012) and/or biomass (Guieu et al. 2005, Paris et al. 2010) combustion particles explain the observed increase in Fe solubility. This discussion is now incorporated in the corresponding section of our revised manuscript.

I do not know that there is evidence of bioavailability of Fe²⁺ or Fe³⁺ in clay minerals, unless they are nano-particles. Fe²⁺ is stable in non-expandable clay minerals, and there is virtually none of it in expandable clays. Ocean basins preserve a clay record which is generally consistent with clay mineralogy and composition in the continental sources, indicating low reactivity.

AR: Regarding the potential bioavailability of Fe²⁺ or Fe³⁺ in clay minerals, note that Journet et al. (2008) leaching tests clearly demonstrated that clay minerals were a main supplier of soluble iron. Others (Cwiertny et al., 2008; Schroth et al., 2009;) also pointed out that Fe²⁺ in clay minerals such as chlorite, but also present in minor amounts in kaolinite, illite and smectites (as we stated with proper referencing in our Ms), was a direct source of soluble iron.

In their assessment of the amount of amorphous Fe phases in the Saharan dust, the authors do not discuss Fe in carbonates: is there any Fe in carbonates? How would this modify the figure of “missing” 0.42 wt% Fe?

AR: Our TEM-AEM analysis of carbonates did not show any Fe. The absence of iron in carbonates is confirmed by the lack of any shifting in the 104 Bragg peaks. Note that replacement of Ca in calcite or in dolomite by Fe²⁺ (Fe³⁺ does not get incorporated in rhombohedral carbonates) results in a reduction in the unit cell, which shifts the Bragg peak position to higher 2θ angles. In the revised version of the Ms we state that carbonates include no Fe, and in the Supplementary Material we now include an EDS spectrum of calcite in the studied Saharan dust showing no Fe (Fig. S6).

Discussion of radiative forcing. This discussion is non-specific and misses some important facts. First, the ms investigates a type of dust event which is not frequent. The amount of time that dust particles such as those described in the ms exist in the atmosphere could be negligible in comparison with the usual atmospheric situation. Thus, the relevance of these data for radiative forcing is questionable.

AR: We now emphasize that the studied extreme dust event is indeed a rare event, whose temporal extension is limited. So its impact on the direct radiative forcing has to be temporally-limited. However, we stress that despite its short time-span, the impact of recurrent extreme events such as the one studied here, as well as those taking place in the Mediterranean area in a more or less yearly basis over the last years (e.g., Avila et al., 2007; Cabello et al., 2012; Titos et al., 2017), can indeed have a significant impact on the atmospheric radiative budget not only regionally but, in the long-term, also even globally. We state so in the revised version of the Ms.

The authors indicate that small particles form aggregates with the large particles. This would mean that the small particles will settle quickly with the large ones and remain suspended only for the short time that the strong winds persist. Second, the authors have no knowledge of particle size distribution vertically in the atmosphere during the dust event; yet, this knowledge is essential to assess the effect on radiative forcing, as they indicate.

AR: We have already discussed that large (coarse and giant) particles can be transported for periods of time longer than 12 h under the strong wind conditions during the extreme event studied here. Regarding the vertical distribution of particle load and size, we have to state that due to turbulent mixing during this event -as well as other major events-, it is very unlikely that particles undergo any kind of size segregation with dust plume height. Indeed the lidar results reported by Fernandez et al (2018) for this event (over Granada) show that there is no significant vertical change in the Ångström exponent (meaning that no significant change in dust particle size

occurs with altitude within the dust plume, which spans from ~1500 m to 3500 m asl). See the image below:

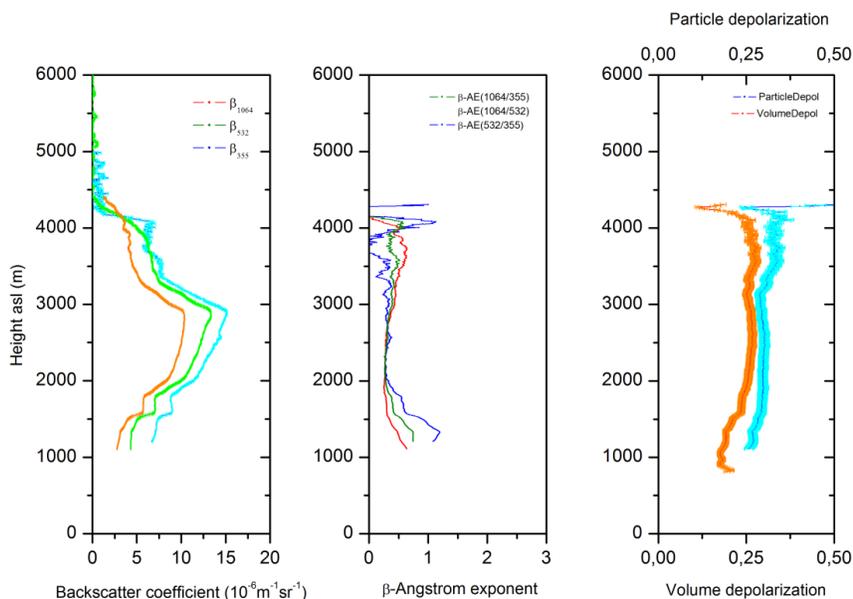


Fig. S7. Backscatter coefficient, β -Ångström exponent, particle and volume depolarization profiles at 12:30 UTC on 22 February 2017 at Granada (From Fernandez et al. (2018) Atmos. Chem. Phys. Discuss. DOI; 10.5194/acp-2018-370).

It is stated that although atmospheric dust generates negative radiative forcing, “internal mixing” of minerals may lead to positive forcing. Why is this? This point is central to the entire discussion and it has to be explained. However, how do the authors know that the mineral particle aggregation that they observe was not produced during the rain that settled the particles? The cementation of mineral particles is mentioned but it is not clear where this knowledge originates. We are all familiar with the strong cohesive forces between mineral particles generated by wetting them and letting them dry; one example of this is the preparation of oriented aggregates for clay examination. If the internal mixing in the dust samples was a result of rain, the particles suspended in the atmosphere would have not been “internally mixed”.

AR: The internal mixing of particles forming heterogeneous aggregates lead to enhanced absorption because there is an increase in the effective refractive index of the aggregate. This is explained in detail by Sokolik and Toon (1999), a study already cited in our Ms. To clarify this point we now state that: " *While an external mixing of (alumino)silicates and iron oxyhydroxide particles in proportions typically found in desert dust has a net negative radiative forcing, their internal mixing can lead to a net positive radiative forcing due to a change in the effective refractive index resulting in enhanced absorption (Sokolik and Toon, 1999).*"

Regarding the mineral aggregation issue, please see also our response to Referee #2 on this specific issue. We are fully confident that our dust particles were already internally mixed in the

atmosphere. Note that clay rich particles such as the Iberulites, which according to Cuadros et al. (2015) form through atmospheric processing and are "cemented" by the strong cohesive forces between (clay) mineral particles generated by wetting and subsequent drying, reportedly, they readily disaggregate when in contact with water (Fiol et al., 2005). Moreover, such aggregates formed due to atmospheric processing are spheroidal, in contrast to the elongated, irregularly shaped, sharp-edged aggregates we observed using FESEM. These points were already stated in our Ms. Moreover, we observed no disaggregation or change in the PSD following intense sonication in water during successive laser scattering analyses, demonstrating that the aggregates were very strongly cemented (i.e., already at the source area), and they did not aggregate during atmospheric processing or during drying after wet deposition. This is further clarified in the revised version of our Ms.

These considerations call for a concise discussion on radiative forcing. In such discussion the authors could point out some mineralogical facts from their samples that may not have been considered in models of dust-radiation interaction, leaving the question open of whether or not they are relevant to the issue.

AR: As indicated above, in the revised version of the Ms. we now emphasize that the extreme dust event is indeed a rare event, whose temporal extension is limited, so its impact on the direct radiative forcing has to be temporally-limited. However, we stress that despite its short time-span, the impact of recurrent extreme events such as the one studied here, as well as those affecting the Mediterranean area in a more or less yearly basis over the last years, can indeed have a significant impact on the atmospheric radiative budget.

Health hazard. This discussion consists on a review of previous studies and an enumeration of aspects that have not been considered in health-mineral studies. Again, the main criticism here is that data from the ms may not be relevant to health issues because they refer to infrequent events. Presumably, people living around the Sahara take shelter during extreme storms. The situation relevant to health is that of habitual, more moderate winds. Instead of pointing out aspects that have not been considered in these studies in the past, it would be more helpful to identify one or two questions learned from this study that may be of interest for health issues, whether or not they prove to be relevant in the long run.

AR: Although this is a rare event, its health impact can be significant. Despite its short-time span, intense dust-events have been demonstrated to have a direct impact of patient hospitalization and death rates (Perez et al. 2008). We thus stress that recurrent extreme events such as the one studied here and those taking place in a more or less yearly basis over the last years/decades, plus the continuous high dust loads in Northern Africa can indeed have a significant health short- and long-term impact. Unfortunately, desert dust-related health effects (e.g., "desert lung", see Middleton, 2017) and mortality peak in the areas around the Sahara (Wang et al., 2016), which is evidence that people living in these areas do not take all the necessary precautions.

Regarding our results, we already made a strong case showing that the presence of abundant micrometer-sized palygorskite fibers associated with iron nanoparticles can have a strong health

impact. That was the ultimate focus of our discussion in this section. Following this referee's suggestion, we conclude pointing out that the possible link between palygorskite-rich desert dust and long-term health effects should be the focus of further research.

At the end of the 1st paragraph in this section there is the assertion that the clay fraction of desert dust has the “most” harmful effects in the short term. This assertion seems to be founded on the studies of health effects of PM_{2.5}. However, as there is no comparison with the effects of other PM values, the conclusion that the clay fraction has the most harmful effects is not supported.

AR: There are numerous studies showing that PM₁₀ has a direct short-term health effect (Perez et al., 2008; Karanasiou et al., 2012) and there are also studies that report that, in comparison, PM_{2.5} appears to have an even more important impact on short-term health effects and mortality (Giannadaki et al., 2014). Indeed, Zhang et al. (2016) (cited in our Ms.) stated "Overall, for respiratory and circulatory mortality, both positive and negative associations have been reported for PM₁₀ of desert dust, but only a positive relationship was reported between PM_{2.5–10} and mortality, and a positive relationship was also reported between PM_{2.5} and human mortality". This was stated in the previous version of the Ms. We agree that the way we stated the possible link between the clay fraction and harmful effect was too conclusive (based on the existing evidence). In the revised version of the Ms. we toned down our statement by indicating: *"These studies suggest that the clay fraction of desert dust can be the one that has the most deleterious effects in the short term."*

In the three sections on relevance, the authors frequently assert that this or that issue or aspect has been “neglected” in previous studies. This is probably not the right word, as it carries a connotation of oversight or incompleteness in such studies. All three issues are very complex and the number of variables is beyond what any single study can consider. In this situation simplifications are necessary and the most relevant variables have to be selected. It would be preferable to indicate that certain analyses of dust composition would help to obtain more realistic results.

AR: We agree that the term "neglected" may have the connotation of incompleteness. Therefore, we have replaced "neglected" with "overlooked", "not considered" or "ignored".

Technical issues

I am not qualified to comment on the investigation of wind trajectories.

P. 13, line 18. Avila et al (1997) did not report goethite, hematite or rutile (?). Of course, the amount of Fe and Ti oxide is small and can be missed in a mineralogical study. However, was not the dust red? If so, how did they account for this colour?

AR: We agree that the red color in "red rains" indirectly indicates the presence iron oxyhydroxide phases... but the point is that these authors did not actually report the presence of the above-mentioned specific Fe-containing phases (i.e., hematite, and goethite), as well as rutile.

Methods. As sample aliquots were treated in different ways, it would be helpful to indicate at the beginning of the description of each technique what treatment the corresponding aliquot had received.

AR: Done. In the Methods section, we now state the specific treatment done to samples analyzed with each technique.

Figure 4. The lower part of the panels, below the maps, is unreadable. Would there be expanded versions of the figures in the final production?

AR: High quality versions of the Figures will be submitted for final publication. In any case, in the pdf version of the Ms. (downloaded from the publisher website), the lower part of the panels in Figure 4 display small captions but they are readable.

Figure 5. There are several questions in this figure. Did the authors carry out background subtraction in the XRD patterns of panels c and d? See that the background is lower to the left of the low-angle peaks than to the right of these peaks (compare with the XRD patterns in panels a and b). Such procedure can deform the XRD pattern significantly in this area and blur the corresponding information. The goethite and hematite peaks are not indicated in panels c and d. It would be helpful to label panels c and d with "clay" and "silt" for an easier identification. The figure contains only information on 2θ , whereas the caption and text use Å: non-frequent users of XRD will find this difficult to follow.

AR: No background subtraction was performed to any of the XRD patterns presented in the figure. The rise in the background at angles 20-30 2θ (best observed in panel (c), sample heated at 550 °C), is simply due to the presence of poorly crystalline and/or amorphous phases. This was already indicated in the Ms (page 13, first paragraph: "Note also that amorphous phases (e.g., amorphous silica -in diatoms- and amorphous iron oxyhydroxides, see TEM results below) can not be detected using XRD, and their content was not negligible as shown by the broad hump at 18-32 2θ in the XRD pattern (Fig. 5a)"). No deformation of the XRD pattern took place.

Regarding the goethite and hematite peaks, they are now indicated in the revised Fig. 5, where panel c and d are now labeled "Clay" and "Silt", respectively. Selected d-hkl values for the main peaks of each clay phase in the dust (discussed in the main text of the Ms.) are now included in Fig. 5c and d.

P. 15, lines 22-25. It is also possible that single sources contain kaolinite of two different crystal orders. The reasons for this can be multiple. Among them, wind and dust deposition form several areas within the Sahara.

AR: We now discuss this possibility too.

Table 2 is completely unclear. It needs to be thoroughly checked for the correctness of the labels and heading. For example, it seems to indicate that the proportion of smectite continually

increases from the clay to the silt fraction and to the bulk, which would be remarkable. Actually, the text in p. 17, line 13, is incompatible with the results in Table 2.

AR: To clarify this point we have included the following in the heading of Table 2: *"Note that the contents of individual clay minerals determined from XRD analysis of the bulk [powder] sample are subjected to a very high uncertainty. More reliable semiquantitative results are obtained from oriented aggregates [OA]."* We also indicate that the Total Silt+Clay fractions row refers to results from oriented aggregates adding "[OA]".

In the main text we now add: *"Note also that because the mass of the silt fraction was 2.06 times larger than that of the clay fraction (results of the hydrodynamic size-separation: sand=2 wt%; silt=68 wt% and clay=30 wt%) the amount of smectites, which along with MLC typically concentrate in the clay fraction, was relatively high in the silt fraction. However, if we consider the unit mass of silt and clay fractions, the amount of smectite in the former (11%) is lower than the amount of smectite plus MLC in the later (15%)."*

Table 4 and p. 20, lines 32-34. The differentiation between smectite and illite-smectite (I-S, or the MLC, mixed-layered clays) is not supported. The authors ground this differentiation on tetrahedral substitution (of Si by Al). Typically, I-S minerals have more tetrahedral Al than smectite, but this is not the only or even most important difference. The central questions are that, in I-S, both the layer charge and K content are higher. Comparing the results for the analyses labelled "smectite" and "I-S" one can see that this is not the case: there are fewer interlayer cations in I-S (this should mean that the layer charge is lower, if the formulas are correct, which I have not checked), and the amount of K is basically the same. According to these data, it is not possible to discriminate between these two groups of analyses as corresponding to smectite and I-S. The results indicate, perhaps, smectite with a wide range of tetrahedral substitution.

The authors mention a beidellitic component in smectite. Beidellite typically has more tetrahedral Al than montmorillonite.

AR: We agree with the referee. We reevaluated every single MLC and smectite analysis (reported in Table S1) and realized that indeed some of the analyses did not comply with a proper MLC, but rather with smectite (and the opposite for the case of some smectite analyses, which were re-assigned as MLC). We have changed Table S1 accordingly and in Table 4 we now report the corrected average structural formulas for both smectite and MLC.

A beidellitic component was considered because the Al content in tetrahedral positions was relatively high in some analyses.

P. 22, lines 1-3. The authors can check their data for a possible contamination of clay minerals with Fe-oxides. Structural formulas of uncontaminated dioctahedral clay minerals should fulfil the following conditions: Sum of tetrahedral cations = 4 (2:1 minerals) or 2 (kaolinite); the sum of octahedral cations is in the range 1.98-2.2; the interlayer charge calculated from the lattice cations is equal to that calculated from the interlayer cations (within perhaps ± 0.01); the interlayer charge

is within the known range for the mineral suggested by the formula. The authors could include the above checks in Table 4.

AR: We checked every single AEM analysis and structural formulae reported in Table S1. Following the suggestion by the referee, and upon a careful analysis of the literature (crystal-chemistry of clay minerals) we have discarded some of the analyses and corresponding structural formulae of palygorskite, smectite and MLC (plus the one from kaolinite already indicated in the previous version of the Ms) either because they include anomalously high Fe contents and/or because they did not fulfilled the conditions listed by the referee. This is stated in the footnote of the revised Table S1. Only analyses that were considered reliable (uncontaminated and fitting compositional ranges for the specific clay minerals) were used to calculate the average structural formulae reported in the revised Table 4. Note that this re-evaluation of our AEM results has resulted in a slightly different value of structural Fe, as well as in the Fe content of palygorskite, smectite and MLC, that have affected the value of calculated "missing iron" (i.e., nanosized Fe-oxyhydroxides). The corrected values are now reported in the revised version of the Ms.

P. 24, top. This is the first time that the authors refer to internal and external mineral mixing, and the meaning should be provided here. The explanation should provide the basis for the relevance that is attached to this difference in further discussion, which is not clear. In my opinion, this is an important point that requires complete clarity in the description of the physical differences between one and the other type of mixing.

AR: To clarify this point, the first time internal/external mixing is mentioned, we now state: "*Note that dust aerosols can be internally or externally mixed. Internal mixing refers to aggregates formed by different mineral particles, while an external mixing involves different mineral particles existing separately.*"

P. 24, line 17: "well-cemented". This is not an observation from FESEM, obviously. Which technique provided this observation?

AR: We already stated that "*They were made up of an aggregate of smaller, well-cemented (i.e., the aggregates were intact after sonication), micrometer-sized particles (Fig. 9b).*" Sonication showed no disaggregation of the large particles, thereby demonstrating that they were well-cemented.

P. 25, lines 8-10. "The samples studied": with what technique? "

AR: With laser scattering (see Materials and Methods). In the revised version of the Ms. we state so.

In agreement with the results from the hydrodynamic size-separation": what were the data?

AR: The results of the hydrodynamic size-separation data (i.e., "(results of the hydrodynamic size-separation: sand=2 wt%; silt=68 wt% and clay=30 wt%)") were already presented in section 3.3. when reporting and discussing the results of the XRD analysis of clays.

Figure 9. The inset spectrum in panel b cannot be read.

AR: We have added labels to each peak so the elemental composition can easily be visualized.

P. 26, lines 2-3. This assertion needs to be supported with a reference or an explanation.

AR: To support this assertion we have cited the classic paper by Sing et al. (1985) where the classification and origins of the shape of gas sorption isotherms are presented.

P. 26, lines 6-9. Is this correct? Why nano-pores should render the dust more reactive than mesopores? Is it related to the area of mineral particles exposed to water/atmosphere? This point needs developing.

AR: According to the International Union of Pure and Applied Chemistry (IUPAC) nanopores in the 5 nm size range are actually mesopores (mesopores are defined as pores with diameter between 2 and 50 nm). Indeed, such mesopores would strongly contribute to the exposed surface area of individual particles and/or aggregates, making them more reactive to atmospheric processing. In the revised version of the manuscript we state: *"The presence of relatively abundant (nano)pores, an aspect of desert dust that has been typically neglected, is of relevance due to their effect on the dust's reactivity, and hygroscopicity because they would strongly contribute to the exposed surface area of aggregates, making them more reactive to atmospheric processing. Such pores could also affect the dust radiative properties (Kempainen et al., 2015)."*

P. 26, last paragraph. Observing the DSC curves in Figure 10, it appears that the sharp peak corresponding to carbonate decomposition starts at ~ 700 °C and ends some degrees above 800 °C. The slope of the DSC curves between 600 and 700 °C is less pronounced and probably due to dehydroxylation events. Also, water is very frequently lost for a range of temperature after the dehydroxylation temperature in clays. Perhaps the authors could recalculate the weight loss in the narrower temperature range indicated above to test whether the resulting carbonate content is then coherent with those of XRD and weight loss after acid treatment.

AR: We fully agree with the referee. The DSC curve clearly shows that decarbonation starts around 700 °C. Our previous studies showed that at a very slow heating rate of 2 to 5 °C/min, decarbonation of calcite starts at ~ 600 °C, but at higher heating rates ≥ 15 -20 °C/min, decarbonation starts at ~ 700 °C (Rodríguez-Navarro et al., 2009). We have recalculated the carbonate content considering the weight loss in the T interval 700-900 °C. The actual carbonate content is 14.7 ± 0.2 wt% (in excellent agreement with the carbonate content determined by XRD and acid decarbonation measurements). This is now stated in the revised version of the Ms.

Description of IR results in pp. 28 and ff. This description has more detail than can be appreciated in Figure 11, and thus the authors could consider shortening it. Several IR bands referred to in the

text are not labelled in the figure. There are several band assignments that need reconsideration or rewriting for a more accurate description. 1) Most, if not all, the IR absorption below 3500 cm⁻¹ (excepting the organic bands) is due to hydration water, so it would be more accurate to say that the band centered at 3400 cm⁻¹ corresponds to water. 2) The sharp bands at 3893 and 3617 cm⁻¹ are from kaolinite; the illite and smectite bands at 3650-3550 cm⁻¹ (depending on composition) are always wider and they can be seen overlapping the 3617 cm⁻¹ band, causing the wide base of this band. 3) The sharp peak at 870 cm⁻¹ is from the carbonates, where this band is always intense. 4) The doublet at 800-780 cm⁻¹ corresponds to quartz, as the authors indicate at some point, and this doublet is always intense. 5) Fe oxyhydroxides frequently have wide bands that are masked by sharper bands produced by other phases. Certainly there is a band overlapping the 800-790 cm⁻¹ doublet of quartz and this could be originated by Fe oxyhydroxide, but nothing of this type is observable near the carbonate band at 870 cm⁻¹. 6) Comparison of the intensity of bands at 1624 and 3400 cm⁻¹, suggests that the band at 1624 cm⁻¹ corresponds entirely to hydration water, and that there is no contribution of carboxylic vibrations here.

AR: Missing bands are now labeled in the revised Fig. 11a. In addition, we have considered the suggestions for band assignment: (1) we now state that " *The broad band centered at ~3400 cm⁻¹ corresponded to ν OH stretching of interlayer (solvation) H₂O of clay minerals, and structural water in ferrihydrite (Russell, 1979)*"; (2) we agree that it is hard to resolve the smectite and illite OH bending and state so in the revised Ms; (3) Similarly, we agree that the 870 cm⁻¹ band also had the contribution of carbonates (we state so in the revised version of the Ms). Note, however, that this band is much more intense than the most intense band of carbonates at 1406 cm⁻¹: it follows that the band at 870 cm⁻¹ has a strong contribution of other phase(s), that is Fe oxyhydroxides (as we stated in the Ms); (4-5) We agree that the doublet at 800-780 cm⁻¹ has a strong contribution by quartz, but the band at 780 cm⁻¹ also has the contribution of OH in ferrihydrite, as we stated in our Ms; (6) It is very difficult to make any quantitative evaluation/comparison between the very broad band of water at ~3400 cm⁻¹ and the OH band at around 1624 cm⁻¹. The absorbance of the OH band, which should be centered at 1644 cm⁻¹ (we state so in the revised version of the Ms), is typically half of the absorbance of the 3400 cm⁻¹ band. In our case the band at 1624 cm⁻¹ is more intense. This is why we stated that in addition to the contribution of the OH bending, this band is also associated with carboxylic groups in organic matter. Note that the bands at 2890-2990 cm⁻¹ confirm the presence of organic matter (in agreement with TG-DSC results).

Figure 11, caption: add "ATR" before FTIR in (a).

AR: Done

Description of results and discussion of FTIR data. The expressions "longwave" and "shortwave" are loose. Wavelength ranges should be used instead.

AR: Done.

P. 30, lines 7-10. These lines should be deleted. First, the authors do not provide the values from Di Baggio et al (2014) so one cannot compare them with those in the ms. Second, absorbance

depends of several variables (particle size, roughness, experimental conditions), none of which is specified. Thus, this text is too vague to be informative.

AR: Done (the lines have been deleted)

P. 30, lines 16-17: What does it mean? What is remarkable about two spectra from Saharan dust looking similar (if this is the meaning of the text)? Perhaps this text can be deleted.

AR: With this sentence we wanted to stress that our experimental UV-Vis spectra were very similar to the wavelength-resolved values of the imaginary part of the refractive index (k-values) of actual Saharan dust samples. Note that measurements of UV-Vis absorbance and k-values are determined using very different experimental and calculation protocols.

P. 30, line 20. In an Fe oxide the ligand is O and the metal Fe, so the text could be more specific indicating "O-to-Fe charge transfer".

AR: We now state: "... with ligand-to-metal (i.e., O-to-Fe) charge transfer transitions (Sherman and Waite, 1985)."

P. 32, lines 9-10: chlorite can be dioctahedral and trioctahedral.

AR: We now state: "*In trioctahedral chlorite iron is incorporated as Fe²⁺ substituting Mg²⁺ in octahedral positions both in the 2:1 structural unit and in the interlayer brucite layers (Weaver and Pollard, 1973).*"

Spelling, etc.

I believe that "thwart" is used mistakenly instead of "dwarf". P. 2, line 25. "Worldwide" would be a more clear word than "global" in this phrase. P. 7, line 27. I believe that the correct reference is Fig. 1b and 1c. P. 9, line 9-10. I think that it would be better to refer to the accuracy of the forecast. After all, the forecast is trying to reproduce the atmospheric events. P. 18, line 22. "matches". P. 23, line 8. I suggest to delete "in situ" as it is not necessary. P. 24, line 21. "clean" is probably not the word to use. P. 26, lines 28-end. This long phrase should be broken up for clarity. P. 30, line 6: delete "terrestrial", as unnecessary.

AR: The suggested corrections has been performed (except the case of "terrestrial" because we consider that this term clarifies the type of radiation we are referring to).

Javier Cuadros