

## ***Interactive comment on “Mineralogy and physicochemical features of Saharan dust wet deposited in the Iberian Peninsula during an extreme red rain event” by Carlos Rodriguez-Navarro et al.***

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### 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,

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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.

### 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.

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

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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. I do not know that there is evidence of bioavailability of Fe<sup>2+</sup> or Fe<sup>3+</sup> in clay minerals, unless they are nano-particles. Fe<sup>2+</sup> 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.

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?

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. 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.

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

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the internal mixing in the dust samples was a result of rain, the particles suspended in the atmosphere would have not been "internally mixed".

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.

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.

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<sub>2.5</sub>. 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.

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.

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## 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?

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.

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?

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  $^{\circ}2\theta$ , whereas the caption and text use Å: non-frequent users of XRD will find this difficult to follow.

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.

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

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in Table 2.

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.

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  $\pm 0.01$ ); 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.

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.

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

P. 25, lines 8-10. "The samples studied": with what technique? "In agreement with the results from the hydrodynamic size-separation": what were the data?

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

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

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.

P. 26, last paragraph. Observing the DSC curves in Figure 10, it appears that the sharp peak corresponding to carbonate decomposition starts a  $\sim 700$  °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.

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  $\text{cm}^{-1}$  (excepting the organic bands) is due to hydration water, so it would be more accurate to say that the band centered at 3400  $\text{cm}^{-1}$  corresponds to water. 2) The sharp bands at 3893 and 3617  $\text{cm}^{-1}$  are from kaolinite; the illite and smectite bands at 3650-3550  $\text{cm}^{-1}$  (depending on composition)

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are always wider and they can be seen overlapping the 3617  $\text{cm}^{-1}$  band, causing the wide base of this band. 3) The sharp peak at 870  $\text{cm}^{-1}$  is from the carbonates, where this band is always intense. 4) The doublet at 800-780  $\text{cm}^{-1}$  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  $\text{cm}^{-1}$  doublet of quartz and this could be originated by Fe oxyhydroxide, but nothing of this type is observable near the carbonate band at 870  $\text{cm}^{-1}$ . 6) Comparison of the intensity of bands at 1624 and 3400  $\text{cm}^{-1}$ , suggests that the band at 1624  $\text{cm}^{-1}$  corresponds entirely to hydration water, and that there is no contribution of carboxylic vibrations here.

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

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

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.

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.

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".

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

Spelling, etc.

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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.

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