

# ***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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Response to Referee # 2

(Authors' Response, AR in blue) (see attached pdf version in color)

Anonymous Referee #2 Received and published: 2 April 2018 General comments: This manuscript reports the mineralogical, chemical, morphological characterisation, as well as number size-distribution and optical properties of Saharan dust collected in intense wet deposition events occurred in February 2017 in Granada. Finally, this

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characterisation is used to discuss the potential biogeochemical implication of dust deposition for supplying soluble iron, the direct radiative forcing of dust and the health impact of dust. The physico-chemical data about transported dust are rare and hence always precious information. However, some shortcuts on the experimental description may question the findings and conclusions of this paper. The manuscript is generally well-written, logically organized, and adequately illustrated. Abstract is succinct and accurate. The analytical work is widespread and careful. However, the discussion about data is often supported by rough approach (see specific comments) and some critical information about protocol are missing, making sometimes the conclusions of this paper unconvincing:

Authors' Response (AR): We thank this referee for his/her overall positive opinion on our study. We also thank this referee for the very detailed and careful review of our study and for pointing out issues that needed to be addressed and for his/her suggestions regarding how the overall quality of the manuscript can be improved. All of them have been addressed. Our answers are presented below (after each comment).

For deposition sampling (p4 and 5), the used protocol is not clear since the authors talk about both wet and dry dust? : “Wet deposited dust was collected at 3 different locations in the urban area of Granada .. In all cases, dry dust was collected (scrapped) directly from clean horizontal surfaces and/or clean ceramic rain/dust collection dishes (21 cm in diameter) with the aid of a spatula and/or a brush. Do you mean that the dry insoluble residue deposited on dishes after wet deposition is collected for analysis? In this case, the dust is collected after evaporation of rain water and it is possible that the precipitation process of salts or amorphous phases happened during this evaporation step. For example, the presence of fibrous calcite could support a potential precipitation. It's critical to detail this step of sampling since a possible precipitation modify all your discussion about the presence of nano-sized ferrihydrite in the collected dust, which is one of finding of this paper. Indeed, the authors argue on a key finding: “a significant fraction of Fe in Saharan dust is already present in the source region as po-

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tentially bioavailable nanosized amorphous and/or poorly crystalline iron oxihydroxides which is Fe is present in dust region as very soluble ferrihydrite"(p33, L34).. If ferrihydrite is very soluble, why do the authors detect it in the particulate insoluble phase of wet dust deposition?

AR. We apologize for the confusion that our poor description of the sampling procedure has created. Actually, we collected the dry residue remaining after the dust dispersed in rainwater (i.e., red rain) was deposited in the collection devices and the rainwater subsequently evaporated (in about 12 h after wet deposition). In no case "wet" samples were collected. Because full evaporation of the wet deposited dust was allowed without any possibility of loss (leaching) of the soluble residue, the finally collected dry dust included both the insoluble and the reprecipitated soluble residue. This is now clarified in the Materials and Methods section of the revised version of the Ms. We are aware that dissolution of a fraction of the most soluble phases (e.g., carbonates, sulfates and nitrates -if present-, as well as amorphous/poorly crystalline Fe-oxyhydroxides) should have occurred when in contact with rainwater. And following drying, such soluble fraction had to reprecipitate. On the one hand, our results show that no sulfates or nitrates were present in the dry residue (again, note that no lixiviation of the aqueous solution took place during sample collection). If such soluble phases would have been present in the original dust, they would be partially dissolved in the rainwater (until saturation) and reprecipitated after drying, and would therefore have been detected. On the other hand, we now present the results of a geochemical modeling using PHREEQC computer code showing quantitatively the fraction of carbonates and iron-oxyhydroxides (goethite, hematite and ferrhydrite), as well as the rest of silicate phases identified, that dissolved in the very small amount of rainwater that fell during the wet deposition event (2 mm, i.e. 2 L per square meter). For this task we considered rainwater with a starting pH of 5.6, at equilibrium with 399 ppm atmospheric CO<sub>2</sub>, reaching equilibrium at pH 8 -computed by PHREEQC and experimentally measured after dissolution of Saharan dust in MilliQ water with starting pH 5.6 -in a wt/vol ratio of 18g dust/2L water- and equilibrated with atmospheric CO<sub>2</sub> at room T. For the case of the carbonates, the amount dissolved in rainwater is 2.3 wt% of the total amount of calcite (no dolomite dissolved because the Ca and carbonate released upon calcite dissolution plus the Mg released following dissolution of a fraction of Mg-containing palygorskite led to saturation with respect to this carbonate). This amount is consistent with the actual amount of dissolved Ca determined by an ion selective electrode following dissolution of the dust in MilliQ water (starting pH 5.6; solid/water ration of 18g/2L) and reaching equilibrium (pH 8). Such a small amount of calcite dissolved and later on reprecipitated during drying cannot be responsible for the formation of the abundant fibrous calcite; the most likely fate of such dissolved amount of carbonate was a limited regrowth of the exiting calcite crystals, because the nucleation of a new carbonate phase would be energetically unfavorable. The same applies for the case of the Fe-oxyhydroxides: PHREEQC simulations considering only the presence of goethite and hematites showed a negligible 3x10<sup>-8</sup> wt% and 9x10<sup>-9</sup> wt% dissolution for the former and later phase, respectively. Simulations considering also the presence of ferrhydrite in addition to goethite and hematite showed no dissolution of the last two phases, and a 0.31 wt% dissolution of the total amount of ferrihydrite. The PHREEQC modeling clearly shows that the amount of dissolved free Fe is almost negligible. Such a solubilized iron cannot account for the amount of amorphous and/or poorly crystalline Fe-oxyhydroxides (ferrhydrite) determined here. Our new modeling and calculations, as well as the results of the new dissolution test, are now presented and discussed in the revised version of the Ms.

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In the same way, if the sampling corresponds to insoluble dry residue of dust, it is important to specify that during the discussion on the chemical composition. Indeed, this implies a potential underestimation of soluble species as Ca, Mg (see Fu et al., 2017) but could also support such of your data for few soluble trace metals (e.g. Fe/Al ratio).

AR. As indicated above, our sampling did not correspond to just the insoluble residue but the combination of the soluble and insoluble residues (i.e., no separation or leach-

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ing of the soluble residue took place).

Moreover, this step of evaporation could also enable the formation of aggregates between deposited dust (formation of crust) and hence modify the distribution between clay, silt, and sand . . . The collection with a spatula or a brush of dust present also a risk to loss of the finest particles (not collected or re-suspended by brush movement).

AR. As indicated above (and stated in the revised version of the Ms) the amount of dissolved (sparingly) soluble phases (i.e., carbonates) that later on reprecipitated during the drying step of the wet deposited dust is very minor. Considering that 2.3 wt% of the total amount of calcite was dissolved and this phase represented only 12 wt% of the bulk dust sample, this means that only about 0.27 wt % of the bulk sample was dissolved and reprecipitated. Such a small amount should not have any significant cementing or coarsening effect on the bulk sample, particularly if one consider that the dissolved carbonate and Ca ions would subsequently be incorporated on the existing calcite crystals contributing to their regrowth. Their reprecipitation as new calcite crystals possibly cementing other dust particles such as clays or tectosilicates is not energetically favorable (simple calcite regrowth is) and it is not consistent with our TEM observations showing individual fibrous calcite crystals not contributing to the cementation of dust particles. Dissolution-regrowth of calcite in the amounts determined here could not be affective for any crust formation leading to an irreversible post-depositional coarsening of the aggregates. On the other hand, regarding the potential selective loss of a fraction of the smaller particles in Sahara dust during the collection stage, we have to state that dust collection was performed with extreme care in order avoid resuspension in the air of the finer particles. Indeed, we observed no dust resuspension during our sample collection. We clarify this point in the Materials and Methods section. The possible causes for the coarseness of the studied Sahara dust (including a possible aggregation during drying of the wet deposited dust) were already discussed in the first version of the Ms, and are further clarified in this revised version (in lieu of the PHREEQC modeling and dissolution experiments, as well as in lieu of the absence

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of changes in the particle size distribution, PSD, following successive laser scattering analyses of dust particles dispersed in water and subjected to intense sonication during PSD analysis).

It's probably not very important for the methods of mass characterisation, but it's more problematic for individual analysis as microscopic observations. For example, that could explain the presence of large particles ( $>10\mu\text{m}$ ) during SEM observations.

AR. See our answers above and our thorough discussion on the textural features that led us to rule out the possibility of coarsening during wet scavenging and subsequent drying of the wet deposited dust (particularly, the lack of spherical aggregates -iberulites-, and the angular shape of the coarse and giant aggregates).

The authors cannot exclude the impact of this potential aggregation on their results even for mass analyses. For example, the question appears since the clay fraction found here is smaller than observed in the literature, even during intense local erosion event (56% in Formenti et al., 2014a) and has to be discussed.

AR. Note that we already stated that due to the extreme intensity of the studied dust event, mobilization of coarser particles took place. Such coarser particles are typically enriched in tectosilicates and carbonates. This helps to explain why the clay minerals in our sample are 47 %, a value which is not so dissimilar to the 56 % reported by Formenti et al., (2014), or the value of 52 % reported by Patey et al. (2015). Moreover, it is well within the range 30-66 wt% reported by the later authors. We state so in the revised version of the Ms.

Without a detailed discussion about these experimental points, the conclusions of this paper could be wrong.

AR. We fully agree and thank again this referee for pointing out these critical issues. See our responses above regarding how in the revised version of the Ms we have clarified the sampling procedure and the related issues.

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Specific comments:

P2, L 30 to P3L5: the authors argue an increase of Saharan dust input and dust plume intrusions in Mediterranean on the basis of various phenomena (drought, changes land uses..). However, recent works seem to emphasize a decrease of Saharan dust deposition in western Mediterranean since the beginning of 2000's due to probably changes of atmospheric circulation (Pey et al., 2013; Vincent et al., 2016..). As the dust deposition is in the heart of this paper, I think that it's important to mention these recent results.

AR. We agree. Indeed, there are indications that changes in atmospheric circulation have an impact on the strength of Saharan dust deposition in the Western Mediterranean, especially those related with a negative summer NAO which led to a recent (2001-2011) decrease in Saharan deposition rates. This is now stated in the Introduction of the revised Ms along with the suggested references.

In general, I found that the bibliography about dust characterisation is a little bit poor. I suggest to include in your comparison with the literature the works on the dust characterisation carried out over Atlantic as e.g. Lazaro et al., 2008; Patey et al., 2015.

AR. In the revised version of the Ms we have included the suggested references on the characterization of Saharan dust over the Atlantic. We want to note, however, that the focus of our research is on an event affecting the Western Mediterranean. This is why we paid special attention to studies reporting on the characterization of desert dust affecting this area.

P5, L15: How the organic matter is affected by the different standard treatments? What is the impact on mass budget of minerals?

AR. The organic matter was analyzed by TG/DSC using the bulk dust samples that were not subjected to any pretreatment. This was explicitly stated when describing the protocol for TG/DSC analyses. The impact of the organic matter (OM) content the

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mass budget of minerals is very minor because the mass of OM determined from TG results is ~0.6 to 1.1 Wt %. This means that if one would consider the OM content to recalculate the mass budget of major and minor mineral phases, only a change in the first decimal would occur (and such a change would be within the standard deviation of the values determined here).

P5, L20: For the analysis, it's not clear if the dust collected on the different locations are mixed or separately analysed. Please precise.

AR. We performed preliminary XRD analyses of each individual sample, observing that no differences among them in terms of phase composition and amount existed. Considering these preliminary results and in order to get a more representative and sufficiently large amount of dust for each of the analysis performed, the three samples collected at the three different sites were mixed prior to the different analyses performed. This is now stated in the revised version of the Ms (Materials and Methods section).

Figure 4: Could you provide forward trajectories from PSA1?

AR. Done. In the same figure (Figure 4) we also present forward trajectories for a Bodélé point source (PSA5)

P18, L2: The chemical composition is for the bulk samples? Please precise.

AR. Yes, the chemical composition refers to the bulk samples. We clarify this in the revised version of the Ms.

P18 from L4: The ratio Si/Al = 3.6 and Ca/Fe = 0.55 in your sample are consistent with dust from Bodélé depression (PSA5) on the basis of Formenti et al., 2014a. This assumption seems to be confirmed by the observations of septa in your TEM analysis.

AR. We performed additional forward trajectory analysis with a source located in the Bodélé depression. The results (see new Figure 4f) show that no dust originating from the Bodélé reached the Iberian Peninsula during the studied event. We now discuss

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so in the revised version of the Ms. Note also that our Ca/Fe ratio is not 0.55 but 1.55., a value to high for a Bodélé provenance. Moreover, the presence of diatoms (i.e., the amorphous silica particles displaying septa observed using TEM), which indeed are abundant in dust entrained at the Bodélé, have been also reported for the case of dust transported from other North African dust source areas. This was already discussed in the previous version of the Ms.

The dust could be originated from a larger zone than only PSA1 and PSA3 (see also Figure 2 for the 22 Feb). Please add a comment about these observations.

AR. We agree: most likely the dust was originated in a larger area, which included PSA1 and PSA3 as main source sub-areas. We indicate so in the revised version of the Ms.

P24, L7: "These results have important implications regarding the possible atmospheric acid processing of the iron-containing phases, as we will discuss below." The calcium nitrate and sulphate formed during atmospheric processing are highly soluble, so it is not surprising the authors did not observe these species onto dust issued from wet deposition sampling. So this result has no important implication. This is not also a good evidence of the "negligible mixing with air masses including anthropogenic derived pollutants".

AR. See our answers above clarifying that the wet deposited dust (i.e., dust plus rain-water) was let to dry and subsequently collected. No leaching of the soluble fraction took place during the process, so no loss of the soluble phases (sulfates and nitrates) would have taken place if these phases were present in the deposited dust. Our observation that no nitrates or sulfates were present has indeed important implications and support our contention that negligible mixing with polluted air masses took place. Such a contention is supported by the Pb/Al ratios and Pb enrichment factors as well as by the V/Al and Ni/Al ratios (now reported). In the revised version we state: "In addition, V and Ni, which are typically enriched in anthropogenic combustion aerosols (Sholkovitz

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et al., 2009), show a V/Al ratio of  $0.1 \times 10^{-2}$  and a Ni/Al ratio of  $0.06 \times 10^{-2}$ . These values are very similar to the corresponding values of the continental crust (V/Al=0.08  $\times 10^{-2}$  and Ni/Al=0.05  $\times 10^{-2}$ ) (Taylor and McLennan, 1985; Sholkovitz et al., 2009)."

P27, L25: Finally, a budget of composition of bulk dust should be provided including carbonate, organic matter and various minerals to give a global view of mass composition.

AR. As stated above, and within the context of TG/DSC results for carbonate phases and OM, we want to emphasize that (i) the impact of the organic matter (OM) content the mass budget of minerals is very minor because the mass of OM determined form TG results is  $\sim 0.6$  to  $1.1$  Wt % and (ii) the recalculation of the carbonate content following the suggestion of referee #1 shows that the content determined using TG (14.7 wt%) is almost identical to that determined using XRD (RIR) (14 wt%). This means that the mass composition (mineral phases) presented in Table 1, would not change (other than the first decimal) if one would include the OM or the TG-derived carbonate contents in a new table. We believe that adding another table with the overall mass composition that almost repeat Table 1, is not necessary.

P31, L16: Several recent works emphasized that the range of solubility of Fe-bearing dust is less than 1% to 80%. Even atmospheric processes increase the iron dust solubility, the highest observed values of solubility are related to the presence of anthropogenic iron (e.g. Sholkovitz et al., 2012). Please modify this part by including the most recent literature.

AR. We fully agree. We have modified this statement considering the results of recent works that emphasize that indeed the most soluble Fe fraction is related to anthropogenic iron. We also indicate that another source of soluble iron is biomass burning (Guieu et al., 2005). We now cite the papers by Sholkovitz et al. (2009, 2012).

P32, L2: "The amorphous and/or poorly crystalline ferrihydrite would thus amount to 28 wt% of the free iron. Åz. This conclusion is based on very rough estimation! so

please detail the calculation (2.04% issued from calculation from Table 4?) and add the uncertainties on the values since on the basis of free iron =  $1.7\% \pm 0.5\%$  of goethite (containing 63% of Fe) +  $0.5\% \pm 0.4\%$  of hematite (containing 57% of Fe, see Journet et al., 2008) =  $1.3\% \pm 0.7\%$ , so a total of iron content =  $3.34\% \pm 0.7\%$ , that is in the range of total iron content =  $3.43\% - 3.69\%$  found by chemical analysis, meaning that no iron is associated to ferrihydrite..

AR. In supplementary material we now present a table with all the input values and results used for the calculation of the Fe content in the different phases. We also explain point-by-point how the calculations to obtain soluble free iron were performed. We have to state that a complete reevaluation of our AEM analyses for the clay minerals has resulted in a more accurate quantification of structural iron. The new value (1.98 wt%) is now used for the calculation of "missing iron". We also made a mistake when calculating the Fe content of goethite plus hematite in our samples (note that the Fe content of hematite reported by Journet et al. 2008, is not correct: the Fe content in hematite is 70 %). This corrected value (1.41 wt%) is now used in our calculations of the "missing iron". Considering these corrected values, we obtain that the "missing iron", that is the amount of amorphous and/or poorly crystalline Fe-oxyhydroxides (ferrihydrite) is 1.3-8.2 % of the total iron (the range of values correspond to the range of total iron determined by ICP-OES and FRX). These results are included in the revised version of the Ms, along with a detailed discussion regarding the implications of these results. Moreover, due to the uncertainty and range of variation of the Fe content determined from AEM and XRD results, we now state "It should be noted that these values, calculated based on the amount of iron in each Fe-containing phase determined by XRD and the Fe content in clay minerals determined from TEM-AEM analyses, are subjected to significant uncertainty. Therefore, the amount of structural and free iron, including the amount of amorphous and/or poorly crystalline Fe-oxyhydroxides (ferrihydrite) presented above are not intended to be purely quantitative results, but a (rough) estimate of the Fe speciation in the studied dust. Nonetheless, these results confirm the TEM observations showing that the amount of nanosized amorphous and/or poorly

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crystalline ferrihydrite is not negligible."

For part 3.8, 3.9 and 3.10: All the discussions need to be re-written by including the reservations in link with sampling protocol about the presence of nano-sized ferrihydrite and size-distribution (See general comments)

AR. Regarding the sampling protocol and its possible effect on the formation of ferrihydrite, see our answer above. Note also that we have now added and discussed the results of a leaching test (performed using two solutions, one with pH 4.7 and another with pH 5.6, aimed at determining (using ICP-OES) the actual value of soluble Fe (fractional iron solubility, FFS), which corresponds to amorphous/poorly crystalline ferrihydrite plus Fe coming from the dissolution of clay minerals. The new data which are presented and discussed support our contention that the contribution of amorphous and/or poorly crystalline ferrihydrite to the FFS is substantial. The new data also show that an additional pool of soluble iron is necessary to account for the  $\sim 20\%$  FFS. In the revised version of the Ms we discuss that such an additional soluble iron comes from the dissolution of clay minerals. The new FFS results enable us to discuss our results in lieu of existing published results for FFS measured in the Mediterranean and North Atlantic areas. Regarding the size-distribution, in section 3.9 we now further elaborate on the possibility that coarsening might be associated with wet scavenging/deposition and the subsequent drying prior to sampling, showing that coarsening during wet scavenging or during drying of the red rain once deposited, is very unlikely.

Minors corrections:

P2, L4: "large" instead of "enormous"

AR. Done

P4, L 20: 48h instead of 42h

AR. Done

P8, L15:  $\mu\text{g m}^{-3}$  instead of  $\mu\text{m m}^{-3}$

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AR. Done

Figure 4: forward trajectory for the 21 Feb should be presented for 50 m instead 500 m.

AR. Done

Table 1: Please precise that the wt% is for "treated dust samples" without carbonate fraction

AR. We already did so: in the bottom of the Table where we stated "This size-fraction powder sample was subjected to carbonate elimination"

P18,L14: Formenti et al., 2014a instead 2014b

AR. Done

Table 3: please precise the uncertainties on measurements for ICP and XRF analysis.

AR. The uncertainties of the ICP and XRF analyses were already indicated in section 2. Methods, subsection 2.3. where we stated: For the case of ICP-OES " The instrumental error is  $\pm 2\%$  and  $\pm 5\%$  for elemental concentrations of 50 ppm and 5 ppm respectively." and for the case of XRF "The quality of the analysis was monitored with reference materials showing high precision with  $1\sigma = 1.0\text{--}3.4\%$  on 16 data-sets at the 95% confidence level."

References: Fu, Y., Desboeufs, K., Vincent, J., Bon Nguyen, E., Laurent, B., Losno, R., and Dulac, F.: Estimating chemical composition of atmospheric deposition fluxes from mineral insoluble particles deposition collected in the western Mediterranean region, *Atmos. Meas. Tech.*, 10, 4389-4401, <https://doi.org/10.5194/amt-10-4389-2017>, 2017. Lazaro, F.J., Gutierrez, L., Barron, V., Gelado, M.D. The speciation of iron in desert dust collected in Gran Canaria (Canary Islands)/combined chemical, magnetic and optical analysis. *Atmospheric Environment* 42, 8987-8996, 2008. Patey MD, EP Achterberg, MJ Rijkenberg, R Pearce - Aerosol time-series measurements over

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the tropical Northeast Atlantic Ocean: dust sources, elemental composition and mineralogy, *Marine Chemistry*, 2015. Pey, J., Querol, X., Alastuey, A., Forastiere, F., and Stafoggia, M.: African dust outbreaks over the Mediterranean Basin during 2001–2011: PM10 concentrations, phenomenology and trends, and its relation with synoptic and mesoscale meteorology, *Atmos. Chem. Phys.*, 13, 1395–1410, doi:10.5194/acp-13-1395-2013, 2013. Vincent, J., Laurent, B., Losno, R., Bon Nguyen, E., Roullet, P., Sauvage, S., Chevaillier, S., Coddeville, P., Ouboulmane, N., di Sarra, A. G., Tovar-Sanchez, A., Sferlazzo, D., Massanet, A., Triquet, S., Morales Baquero, R., Fornier, M., Coursier, C., Desboeufs, K., Dulac, F., and Bergametti, G.: Variability of mineral dust deposition in the western Mediterranean basin and south-east of France, *Atmos. Chem. Phys.*, 16, 8749-8766, 10.5194/acp-16-8749-2016, 2016. AA. All of these references are no cited and listed in the reference section.

Please also note the supplement to this comment:

<https://www.atmos-chem-phys-discuss.net/acp-2018-211/acp-2018-211-AC2-supplement.pdf>

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Interactive comment on *Atmos. Chem. Phys. Discuss.*, <https://doi.org/10.5194/acp-2018-211>, 2018.

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