

## Paper acp-2014-190 by Formenti et al.

I would start by thanking the referees for useful comments and suggestions which surely improve the readability and the significance of the paper. We have tried and addressed their comments at the best of our possibilities.

However, I would like to state by disappointment regarding the form of some of the comments on the English. We are clearly not English native speakers and we acknowledge the fact that our writing needed to be improved. However, I do not understand why this point has not been raised in the first technical phase of the review, where it was most appropriate. In this phase, confidential, the manuscript has been evaluated as “excellent” in all the criteria, including the presentation. It is difficult to understand, that the status of the presentation has changed to such an extent between the confidential and the public phases.

### Answers to Anonymous Referee #1

Line 404: Should be Equation (2)

Done

Line 799: “In this purpose..”=>”For this purpose...”

Done

Line 885: “..than over transport zones” => and at some distance”

Done

Line 906-907: “Laurent et al., 2008)...Klaver et al., 2011).”=> “Laurent et al., 2008; Ginoux et al., 2012), and in attributing an origin to transported dust (e.g. Klaver et al., 2011).”  
Ginoux, P., J. M. Prospero, T. E. Gill, N. C. Hsu, and M. Zhao (2012), Global-scale attribution of anthropogenic and natural dust sources and their emission rates based on MODIS Deep Blue aerosol products, Rev. Geophys., 50, RG3005, doi:10.1029/2012RG000388.

Done

Lines 908 to 915: Sentence too long. Unclear.

This sentence has been rewritten as “Beside the uncertainties inherent to the detection of sources, there are two additional factors of ambiguity in source attribution: first, air masses, especially during winter-time, mostly travel in the boundary layer and might uplift dust aerosols at various times before reaching the sampling site; secondly, aircraft samples might integrate transport from various sources active at the same time due to the fact that aircraft moves during sampling and that sample collection lasts at least 20 minutes, which corresponds to about 120 km at typical aircraft cruise speed (see Figure 1 in Chou et al., 2008 and Figure 1 in Klaver et al., 2011).”

Line 917: “from the natural mixing that occur in the atmosphere during transport.”=>”from atmospheric mixing occurring during transport.”

Done

Line 941: “...with the estimate of parameters which are relevant ...”=>”estimate of parameters relevant...”

Done

Line 942: “...on the ocean productivity”=>”on ocean productivity”

Done

Line 946: “...this overcomes...”=>”...higher than...”

Done

Line 947: "...has little correspondence with the model proposed by the OPAC database." => "... is quite different from the OPAC database."

Done

Line 976: "impacting the refinement of the" => "impacting our"

Done

Lines 1009-1020: Need editing for proper English.

This sentence has been rewritten as "Regarding the iron fractional solubility, our data are not conclusive in identifying a clear regional difference with respect to the variability observed for dust collected over the Atlantic Ocean after short- and long-range transport. This limited regional variability suggests that a single reference value (0.1%) of the fractional solubility SFe of Saharan and Sahelian dust before atmospheric transport could be used in biogeochemical models. Direct field measurements of SFe close to emission sources, unavailable at the moment, are needed to confirm this finding. Finally, the SFe value estimated for dust near source regions is in the lowest range than values obtained for dust collected over the Atlantic Ocean, pointing to the need of taking atmospheric processing into account when iron solubility is ought to be described at the global scale. "

Tables: I would recommend adding a table containing typical values for each source regions of the real and imaginary parts of the refractive index at 370, 440, 500, 700, 9600 nm, as well as soluble Fe. This is the main objective of the paper.

The main objective of the paper is to relate on the regional variability of the mineralogical composition of mineral dust. The complex refractive index and the Fe fractional solubility have been calculated to give an idea of the relevance of this regional variability (or its absence). So we do not feel it is necessary to

Figure 9: The caption should be rewrite as "Normalized volume size distribution  $dV/d\log(EOD)$  at Banizoumbou during 3 days in summer (J1 red line, J2 green line, J3 blue line) and winter (black line),..." Change the colors accordingly, as they cannot be distinguished in the actual Figure.

Done

Figure 11. "Figure 11.a represent the real part.." In my version Figure 11.a represents the imaginary part of the refractive index.

This is now corrected.

Figure 11. I don't understand why the imaginary part of the refractive index for Sahelian dust is smallest. This does not correspond to your analysis. You showed that Sahelian dust contains the highest iron content. You have either an error in your Figure or you will need to explain this inconsistency.

It is not surprising when thinking to the differences in the matrix. Sahelian dust has the highest content of no or little-absorbing minerals (kaolinite, quartz), which constitute 80% or more of the particle volume, the lowest content of illite (slightly absorbing), and no calcite.

### Answers to Anonymous Referee #3

2) Many of the results presented and discussed in the paper are related (or partly related) to the effects of soil weathering. I refer to figures 3, 6, 7 and 8. The relative proportions of Ca, Fe and Fe oxides and TiO<sub>2</sub> are partly related to soil weathering at sources. The Sahel is highly weathered, showing low amounts of Ca, higher amounts of Ti and iron oxides. Surprisingly there is no reference to these well-known processes.

I recommend the authors to read the publications of Shi et al (2011 and 2012) and I ask them to enrich the discussion of the results.

Shi, Z., et al. (2011), Influence of chemical weathering and aging of iron oxides on the potential iron solubility of Saharan dust during simulated atmospheric processing, *Global Biogeochem. Cycles*, 25, GB2010, doi:10.1029/2010GB003837.

Shi, Z., Michael D. Krom, Timothy D. Jickells, Steeve Bonneville, Kenneth S. Carslaw, Nikos Mihalopoulos, Alex R. Baker, Liane G. Benning, Impacts on iron solubility in the mineral dust by processes in the source region and the atmosphere: A review, *Aeolian Research*, Volume 5, August 2012, Pages 21-42

The paper is mainly focused on the mineralogical composition of dust. The chemical/mineralogical relation between the aerosol and parent soils is one of basis of the identification of sources. In consequence, it is difficult to talk about the effect of soil weathering on aerosol composition since it is one of our working hypotheses (section 3.1.). However, to clarify the difference of mineralogical composition of parent soils in the introduction and to mention the difference of soil weathering, we have added a sentence add in L15 P10245:

“The mineralogy of the Saharan and Sahelian source areas have different mineralogy: the Sahara is mainly composed by calcisols or arenosols, whereas the Sahel is richer in weathered plinthosols (Fe oxides/kaolinite/quartz) (Pye, 1987; Claquin et al., 1999; Caquineau et al., 2002; Nickovic et al., 2012; Journet et al., 2014). As a consequence, mixing or layering of dust transported from the Sahara and locally emitted by convection over the Sahel should be detectable through differences in the composition over the atmospheric column. “

3) Related to the previous point. I have my concerns about the validity of the assumptions in section 4.2.2. The section assumes that iron in aluminosilicates control iron solubility in dust. This section is written as if this is not an assumption but something proved. There is quite a lot of debate in the literature in this respect. I again refer to Shi et al. (2012) for this discussion. I am not asking to change the section. I am asking the authors to balance and discuss this assumption acknowledging other points of view. It is not clear that aluminosilicates control iron solubility. Nanometer-sized iron oxides in poorly weathered soils may be also important. This should be noted and discussed in.

To balance the discussion on the minerals which are providers of soluble iron, we add a sentence in L15 P10272: " Moreover, Shi et al. (2011) mention the presence of highly-soluble nanoparticles of ferrihydrite or poorly crystallized iron in fine fraction of soils. However, the quantification of this iron phase is obtained by sequential extraction and is difficult to apply on field samples due to the low mass. So we are not able to consider this species in our calculation.”

### Answers to Anonymous Referee #3

My only major remark is that the authors claim to base their provenance studies on back trajectory calculations and satellite imagery, but this is never detailed and no examples are given. It would be great to add for example a map showing the identified source areas by back trajectory calculation for all samples to compare them with the prescribed PSA from earlier investigation (like Chou et al. 2008 have done for their single samples).

We understand this remark but, as Referee #3 also says, the identification of the source areas by samples has already been presented in previous papers. We feel this will be a repetition and would increase even further the already large size of the manuscript.

For particles larger than 10  $\mu\text{m}$  under atmospheric turbulent conditions the referred to 'standard' formulas might be less than optimal, in particular when considering wind speed fluctuations. The referred Rajot et al. 2008 call their estimates 'preliminary'. Was this inlet ever since characterized?

No extensive numerical modelling has been performed to fully characterize the inlet transmission efficiency. It is surely possible that we missed some coarse particles on the samples during convective events. This is surely a point that will need to be addressed in future work.

10254/13-10255/4 and 10256-10257: Soil/dust might be constituted by non-negligible amounts of soluble matter like chlorides and sulfates (e.g., Osada 2013). Can this be excluded here? Osada, K. (2013): Water soluble fraction of Asian dust particles. doi: 10.1016/j.atmosres.2013.01.001

We have measured the elemental composition for all our samples and found very minor traces of Cl and S. Cl and S-bearing minerals can therefore be neglected from the composition of our samples.

10260/24: On which information does this impression rely? If there was any evidence for dust emission by satellite or other means, it should be stated and, accordingly, PSA3 / PSA4 source dropped from the paper in favor of an NN source.

The reviewer is right. For some samples, back-trajectories showed that air masses got in contact with the surface over North Niger and satellite (IDDI images), in that case we labelled the origin as PSA3-NN or PSA4-NN. We therefore modified the sentence as follows "The PSA4 was sampled on a few occasions during wintertime. As for PSA3, samples originating from PSA4 for which the air masses had got in contact with the surface in northern Niger when satellite images indicated emissions, have been labelled as PSA4-NN".

10261/14-end: If I get it right from the text, data points in Fig. 3 are colored according to their source region. However, a strict division at the 3.0 value at each axis is visible, without a single outlier (except the orange ones). This value of 3.0 is in the text then referred to as distinction criterion. It is hard for me to believe that an atmospheric sample series (measured by methods containing considerable uncertainties in the percent range, as detailed by the authors) can come along without a single outlier. Please comment on that. If the elemental ratios were used (also) for discrimination, the graph doesn't support really the statement on a provenance-composition link without a more detailed explanation, also of the ancillary data.

The reviewer is right, the presentation of the data is misleading. The value of 3.0 is not an imposed threshold, but it is the value around which the most of the data separate between samples of Sahelian dust with respect to Saharan dust. We have checked again carefully all the attribution for the data points, and actually found a few cases (7) for which the attribution is ambiguous and the origin of dust could be either Sahelian or Saharan. We have therefore modified Figure 3 to take into account this ambiguity.

10262/7-21 and Fig. 4: Albite and orthoclase are two of the endmembers of the ternary feldspar phase diagram. Though there are not extremely rare species, with respect to former analyses (see the cited Schuevans review and its references) it must be doubted that these two were the only feldspars present in the dust all the time. As XRD calibration factors in Table 1 are listed only for these endmembers, my concern is that the XRD spectrum interpretation was considerably biased by the lacking degrees of freedom with respect to other minerals, i.e. only these two feldspar minerals were allowed. If this was the case, the retrieved mineralogical composition should be considered as an indicative-only model composition.

No, actually albite and orthoclase are the only two feldspars detected in our samples.

10264/5-7: As I'm not familiar with the used Fe analysis techniques: can this type of analysis identify only goethite and hematite? What happens when other Fe minerals are present, e. g., magnetite - will they be attributed to one the two or neglected?

The XANES analysis can identify also other Fe-minerals depending on the inflection points of their absorption spectra. O'Day et al. (2004) presents the XANES spectra of various Fe-bearing minerals, including Fe oxides (Figure 1.c). Whereas the position of the inflection points is very similar for goethite, hematite and magnetite, the relative proportions of the peaks in the absorption spectra are different.

As presented in Formenti et al. (2014b), a model considering goethite, hematite, illite and smectites allows reproducing by a linear combination fit the absorption spectra measured for the real samples.

It should not be forgotten than, as discussed by Lazaro et al. (2004), magnetite accounts for less than 7% of the total iron in aerosol dust samples. This is of the same order of magnitude that the errors of the fit taking into account the differences between the minerals in their standard and in their real forms.

Lazaro, F. J., et al., The speciation of iron in desert dust collected in Gran Canaria (Canary Islands): Combined chemical, magnetic and optical analysis, *Atmospheric Environment* 42 (2008) 8987–8996

Formenti, P., et al., Dominance of goethite over hematite in iron oxides of mineral dust from Western Africa: quantitative partitioning by X-ray Absorption Spectroscopy, under revision for *J. Geophys. Res.*, 2014

10264/22: As elevated Ti contents go along with local erosion, and local erosion probably goes along with larger grain sizes, can the observed lower Ti content in transported dust then be related to a grain size effect by large-particle removal during transport?

This is a possible explanation; however, we do not have any element to corroborate it. Nonetheless, it should not be forgotten than titanium oxides can be found both in the fine and the coarse fraction, and isolated titanium oxide particles, often associated with iron oxides are smaller than 200 nm.

10266/13-16: If the size distributions are available also in absolute concentrations instead of relative, by comparing the relative volume/mass loss with the shift in composition from quartz to clays, this argument could be strengthened (if the numbers agree).

I understand this; however, this cannot be implemented as the different samples are characterized by different total concentration.

10269/1: 'simplified to few minerals, clays, . . .': Please note that there are hundreds of different clay minerals, so the simplification here mainly derives from the usage of the very generalizing notion 'clay'.

We have replaced "clays" by illite, kaolinite and smectite clays, which are the clay species which we observed in our samples.

10270/19: As the wavelength-position of the absorption bands is given by the crystal structure, why should there be a variation?

The band position can be modified also by the particle shape, see Figure 3 in Hudson et al. (2008).

Hudson, P. K., E. R. Gibson, M. A. Young, P. D. Kleiber, and V. H. Grassian (2008), Coupled infrared extinction and size distribution measurements for several clay components of mineral dust aerosol, *J. Geophys. Res.*, 113, D01201, doi:10.1029/2007JD008791.

10277/27-29: From which database the real part was taken for that paper? If I refer to mineralogical databases (mindat.org, webmineral.com), the real parts of the refractive indices of the major components for visible light mostly range between 1.53 and 1.57, so the lower values listed here (for the first time) are somewhat surprising.

The reference papers for refractive index used in this manuscript are reported in Table 4. For illite and kaolinite in the UV-visible part of the electromagnetic spectrum, we referred to values reported in Egan, W. G. and Hilgeman, T. W.: *Optical Properties of Inhomogeneous Materials: Applications to Geology, Astronomy, Chemistry, and Engineering*, Academic Press, 235 pp, 1979.

These authors report that, between 370 and 950 nm, the real part of the refractive index is of the order of 1.42-1.43 for illite and in the range 1.49-1.51 for kaolinite. These two minerals constitute the largest fraction of the mass in our samples, so it is not surprising that the real part of the refractive index of the global aerosol reflects these lower values.

10255/23-25 and Fig. 1: If it is easily possible and you mention it in the text, I suggest marking the measurements with local erosion separately, as it would enhance this (otherwise not too interesting) graph.

This is now done

10258/21-27: While still no exhaustive assessment, Jeong (2008) has made some points on that. That might be a useful reference here, even though he used Asian dust. Jeong, G. Y. (2008): Bulk and single-particle mineralogy of Asian dust and a comparison with its source soils. doi: 10.1029/2007JD008606

To take this suggestion into account, we have added the following sentence "Jeong (2008) has shown that the calcite and the K-feldspar fractions are very similar in Asian dust and the corresponding silty soil fraction. The percent of phyllosilicate is higher in the dust aerosols than in the soil, whereas the quartz and plagioclase fractions are lower".

10260/5: Glaccum

Done

10262/5: diverse?

Sentence has been rewritten as "This dataset represents a diversity of sources and emission conditions"

10262/9: Please be aware that the French 'orthose' is 'orthoclase' in English. Occurs multiple times, e. g., also in Table 1 and Fig. 4 and other Figures

Done

10262/18-20: rephrase sentence.

This has been rewritten as "We can obtain the mass fractions of minerals which can be detected by X-ray diffraction by using the calibration factors as described in section 2.3.2 (Figure 4). "

10263/20: subsets

Done

10264/20: I was not able to find a comment on Ti substituting anything in the referred Chou et al.

Indeed, the sentence is not clear. The paper by Chou et al. does not reference the substitution of Ti in aluminosilicate, but the fact that Ti is observed in individual aluminosilicate particles.

We rewrote the sentence as follows

“This should be considered as an upper limit estimate as some of the titanium in mineral dust is present as substitution element in aluminosilicates (Dolcater et al., 1970).”

10265/7: By combining?

Done

10268/6: weight

Done

10270/16: shows

Done

10278/10: but calcite is also transparent

We used the refractive indexes of Querry et al. (1978), according to which the imaginary part of the refractive index is of the order of 0.05.

Table 1: Are the percentages given in parentheses the relative uncertainties? What is given as uncertainty? Please indicate.

The caption of Table 1 has been changed as follows “Table 1. Calibration coefficients by mineral obtained from the calibration of the XRD analyser used in this study. The calibration coefficients represent the slope of the linear correlation between the number of diffracted counts by unit mass. The references of the standard minerals used in this study are also reported. The absolute uncertainty on the slope is also indicated, whereas numbers in parenthesis are the percent uncertainty obtained as ratio between the absolute uncertainty and slope value.”

Table 2: I suggest dividing the first column from the second and third or using another unit (fraction instead of percent). Maybe first column header could be ‘oxide fraction of total Fe’.

The caption of Table 2 has been modified as follows “Mean percent values of the oxide fraction of total Fe and relative proportions of hematite and goethite to total iron oxide as obtained by XAS/XANES analysis. Standard deviations are indicated in parenthesis.”

Fig. 1: x-axis must be labeled with ‘ $\mu\text{g}$ ’ instead of ‘ $\mu\text{m}$ ’. I suggest scaling both axes on same length to produce a square graph. Please indicate whether the dashed line is 1:1 or the calculated regression.

The x-axis labelling has been modified, and the x- and y-axis now have the same length.

Fig. 3 Caption: should read ‘DODO’? If the long paper list in parentheses doesn’t contain any new data over the Formenti 2011a/Scheuvens 2013 dataset, it should be omitted. Gray levels are hard to distinguish.

Done

Fig. 11 Caption, line 2: originating?

Done