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Interactive comment on "Distinct chemical and mineralogical composition of Icelandic dust compared to North African and Asian dust" *by* Clarissa Baldo et al.

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Referee 1 - Anonymous

We thank the reviewer for the positive comments to this manuscript. Here we respond to specific comments point by point.

Comment 1: Materials and methodology. Page 4, lines 115–116: "The method in Di Biagio et al. (2017), allowing for the realistic generation of dust aerosols from parent soils, was adopted for the dust particles generation." Page 4, lines 123–125: "CESAM (French acronym for Experimental Multiphasic Atmospheric Simulation Chamber), a

4.2 m3 stainless steel atmospheric simulation chamber (Wang et al., 2011), was used to generate the PM20 samples while acquiring information on the size distribution and the optical properties of the generated dust aerosols." Two different chambers were used to resuspend soils. Comment: The method in Di Biagio et al. (2017) allows for the realistic generation of dust aerosols from parent soils, how about CESAM? Are the physical and chemical characteristics of the sand and dust generated by these two chambers the same?

Response: a) We are sorry for the confusion, Di Biagio et al. (2017) used CESAM to generate dust particles.

These paragraphs have been modified according to the referee's comments: Line2 110-137: The PM10 samples were used for offline composition and mineralogy analyses. PM10 was collected using a custom-made reactor schematically represented in Figure S1. The method in Di Biagio et al. (2017) was adopted to generate dust particles, allowing for the realistic generation of dust aerosols from parent soils. Firstly, the sediment samples were sieved to < 1 mm to remove the non-erodible fraction. 15 g of sediments were placed in a Büchner flask and flushed with pure nitrogen for 10 minutes to eliminate gaseous contamination and residual water vapour. The sample was then shaken for 5 minutes at 70 Hz on a sieve shaker (Retsch AS200) and injected in a glass manifold of approximately 1 L by nitrogen gas at 10 L min-1, while the air was pumped at a flow rate of 30 L min-1 into a PM10 sampling head (custom-made). The PM10 fraction was collected on 0.4 μm polycarbonate filters and transferred into centrifuge tubes. The system was manually cleaned prior to each loading and flushed for 5 minutes with pure nitrogen to ensure an initial particle-free environment. The PM20 fraction was collected using the large-scale atmospheric simulation chamber, CESAM (French acronym for Experimental Multiphasic Atmospheric Simulation Chamber) (Wang et al., 2011). The CESAM simulation facility, made of stainless steel, consists in a 4.2 m3 multi-instrumented environmental chamber which allows to measure the size distribution and the optical properties of the generated dust aerosols

while collecting filter samples for offline analysis (Di Biagio et al., 2017; 2019). Dust particles were generated with the sieve shaker (Retsch AS200) using the same protocol as for the small reactor as in Di Biagio et al. (2017), and injected in the CESAM chamber by flushing a Büchner flask with nitrogen gas carrier at 10 L min-1 for 10 minutes. The dust aerosol injected in CESAM was left suspended for about 10 minutes to allow the particle mass concentration inside the chamber to become spatially uniform. Dust particles corresponding to approximately the PM20 fraction were extracted from the chamber using custom-made filter samplers as in Caponi et al. (2017). Particles were collected by filtration on 0.4-μm pore size polycarbonate filters of 37 mm diameter at 7 L min-1 for approximately 1 hour. The residence time of particles in the chamber depends on their size. As shown in Di Biagio et al. (2017), particles larger than 1 μm have a lifetime of 20-30 minutes, while the lifetime of particles smaller than 1 μm can exceed a day. A second filter sample was collected successively to the first one to verify if the chemical composition of the dust was dependent on size. No significant difference was observed (not shown). The relation between the composition, size distribution and optical properties of the aerosol dust will be the subject of a companion paper (Baldo et al., in preparation).

b) The PM10 resuspension apparatus was used to collect dust particles primarily to determine the chemical composition, mineralogy, and Fe speciation in the samples. The XRF measurements conducted on both the PM10 and PM20 fractions showed that these have very similar chemical composition. Page 9, line 165-268: "The XRF measurements showed that the difference between PM10 and PM20 in element oxide content > 1% including CaO, Fe_2O_3, Na_2O, MgO, Al_2O_3, SiO_2 and TiO_2 is within 16%. For Fe_2O_3, Al_2O_3, SiO_2 which are the major element oxides in the dust samples, the relative differences in content are <10%".

Comment 2: Comparison of Icelandic dust with North African and Asian dust. Page 12, lines 357-359: "TiO_2 catalyses heterogeneous photochemical reactions of atmospheric trace gases including SO_2, NO_2, VOC and O_3, and contributes to the chemical balance

of the atmosphere (Chen et al., 2012). In North African and Asian dust, TiO_2 is around 1% (e.g., Formenti et al., 2014b; Jeong, 2008; Shi et al., 2011b), which is significantly lower than that in Icelandic dust (2-5.5%)." Comment: Titanium dioxide (anatase and rutile) can serve as photocatalyst in oxidation and reduction reactions. However, TiO_2 given by XRF is not the mineral of TiO_2, but element Ti. The high content of element Ti in dust does not mean that it contains higher TiO_2 minerals.

Response: This paragraph has been modified according to the referee's comments: Lines 357-359: TiO_2 catalyses heterogeneous photochemical reactions of atmospheric trace gases including SO_2, NO_2, VOC and O_3, and contributes to the chemical balance of the atmosphere (Chen et al., 2012). In North African and Asian dust, TiO_2 is around 1% (e.g., Formenti et al., 2014; Jeong, 2008; Shi et al., 2011). In Icelandic dust, the element oxide concentration of Ti is relatively high 2-5.5%, although Ti can be not just as TiO_2 minerals (anatase and rutile). Ti may be present in magnetite and aluminosilicate minerals (e.g., augite) or in the amorphous glass.

Referee 2 – Kandler

We thank Dr. Kandler for providing constructive comments. We addressed each of the comments point by point below.

Comment 1: Table 1: the shown CIA values do not agree with the formula given in line 185 and the oxide weights in the table. E.g., the CIA in the first line is 51. Recalculate. 385/390: Adjust the statements. Figure 7 + 8: Adjust the plot and in case conclusions.

Response: Thank you for pointing this out. We apologize for making a mistake in the formula used to calculate the CIA. The CIA was calculated according to the formula in Price and Vebel 2003, thus the major element oxides are not as molar fractions but as molecular proportion of the element oxides. This has now been modified (Please see response to comment 3).

Comment 2: 186: How can the CIA defined the given way become larger than 100?

Response: That was another mistake, 100 is the optimum weathered value.

Comment 3: 190: Please remove the comments related to PIA and CIW, as they don't seem to be used

Response: The Chemical Weathering Index paragraph in the methodology section, lines 180-192, has been modified according to the referee's comments: Chemical weathering index The degree of chemical weathering of Icelandic dust was calculated based on the elemental composition. This is important to evaluate the presence in the samples of secondary minerals such as clays. The chemical index of alteration (CIA) (Nesbitt and Young, 1984) was considered most suitable for the present datasets based on the chemical compositions. The CIA is interpreted as a measure of the degree of weathering of aluminium silicate minerals, (in particular feldspars) into clay minerals. In this study, the CIA was calculated according to Price and Velbel (2003) using the molecular proportion of the element oxides which were obtained by dividing the weight percentage of each oxide by the molecular weight of the oxide:

$$CIA = (Al_2 O_3)/(Al_2 O_3 + CaO + Na_2 O + K_2 O) \times 100$$

CIA $\leq$ 50 represents the optimum fresh value, while 100 is the optimum weathered value. The CIA uncertainty was estimated using the error propagation formula and is $\sim$14%.

Comment 4: 140: Why was PM20 less than PM10? That doesn't seem to be logical without further explanation.

Response: We should have made this clearer, PM20 and PM10 samples were collected from two different chambers and with two different samplers (the flow rate also differs). The mass concentration in the two collection systems is considerably different. The PM20 fraction was collected using CESAM, a 4.2 m3 stainless steel atmospheric simulation chamber at a flow rate of 7 L min-1. In the dust resuspension apparatus PM10 is collected at a flow rate of 30 L min-1, and the volume of the reactor is around

1 L. Line 140 has been modified according to the referee's comments: Line 140: PM20 samples were not analysed because the mass of dust particles collected from CESAM was not sufficient for the XRD analysis. This is because the mass concentrations in the CESAM chamber is much lower compared to the custom-made reactor for the PM10 collection.

Comment 5: 150-152: How can a mineral (augite) be chosen as reference for an amorphous matter in XRD?

Response: In this study, the chemical composition of the glass fraction in the Icelandic dust samples is unknown. However, the samples MIR45 is mostly amorphous, and showed similar chemical composition to augite. In our method, we consider the amorphous phase as the augite phase but with poor crystallinity. To support our choice, we observed that the main diffraction peak for the augite phase was at the same position as the amorphous contribution in the diffractograms. In practice, the mineral phase of augite identified using the Highscore Plus 3.0 software was modified in MAUD to amorphous phase by broadening its diffraction peaks following the method in Lutterotti et al. (1998), and saved as reference.

Comment 6: Table 2: Why was the uncertainty for anorthite calculated differently? Why is the chi square for H55 so much higher? Apparently the spectrum fit was worse – missing minerals?

Response: Page 5, line 152: "The Rietveld model refines n -1 phases. As the total is fixed to100, the last phase results from the subtraction of the sum of the n refined phases". In this study, using the MAUD software, for all the samples the anorthite phase results from the subtraction of the sum of the other refined phases. Since the weight ratio of the anorthite phase are not refined, the corresponding uncertainty is not calculated by the software. Thus, the uncertainty for anorthite were calculated using the error propagation formula.

The higher chi square values obtained for the samples H55 may be mainly due to

missing mineral phases. X-Ray Diffraction (XRD) is a global analysis that requires a minimum number of crystals for each phase, so phases which are less than about 2 or 3 wt.% may not be characterized by XRD. It can be difficult to clearly distinguish minor phases because of wide and overlapping peaks and low diffraction intensity. In addition, when the chi square is close to one, there is no guarantee that the model is correct. In particular, when a large percentage of the intensity comes from the background, this can give relatively small chi square values (Toby, 2006). Thus, "in this study, the quality of the fitting was evaluated considering the chi square, and by comparing visually the observed and calculated diffractograms to obtain a realistic chemical model (Toby, 2006)", Page 5, lines 154-156. H55 is the most crystalline sample and compared to the other samples having chi square values very close to one, its diffraction intensities are considerably higher than the background signal. Lines 154-157 have been modified to highlight this: Lines 154-157: The quality of the fitting was evaluated considering the $\chi 2$ calculated by the model close to one, and by comparing visually the observed and calculated diffractograms to achieve a realistic chemical model (Toby, 2006). Small $\chi 2$ values can be obtained when a large percentage of the intensity comes from the background (Toby, 2006). For example, the estimated $\chi 2$ for H55 is relatively high (2.3-3.8) primarily due to missing minor mineral phases. However, H55 has the lowest fraction of amorphous material and compared to the other samples having $\chi 2$ values very close to one, its diffraction intensities are considerably higher than the background signal.

Comment 7: 332-333: While the fractionation is surely lower than the one observed in the hot deserts, at least for the H55 there is some with respect to microcline and glass. Maybe because Hagarvatn is a lake and might have longer residence time of sediments, similar to the hot desert hot spots?

Response: Yes, there is some fractionation in H55. Actually, the Hagavatn sediments are reworked materials from crystalline lava that were previously (at least partly) on the surface. The glacier advanced over the lava, abraded it, and subsequently retreated. Other samples are almost entirely derived from glacial abrasion of hyaloclastic mate-

rials, thus being more "uniform" and having much smaller crystalline component. Line 332 has been modified to highlight this: Line 332: Mineralogical fractionation is not evident in Icelandic dust, probably due to the low chemical weathering, and the lack of larger mineral grains such as quartz, K-feldspar, and clays. Only the more crystalline samples from Hagavatn showed some fractionation with respect to K-feldspar and glass, while the sediments from the other sites are derived from the glacial abrasion of hyaloclastite and thus, they tend to be more uniform.

Comment 8: 171-175: XRF determined elements. Why is oxide weight calculated, if iron content then is back-transformed from the oxide weights? Apart from that, is Fe2O3 a reasonable assumption for Icelandic dust?

Response: Yes, XRF determines elements. It is a common practice to calculate the oxide weight in geoscience (Formenti et al., 2014; Formenti et al., 2011; Lafon et al., 2006; Linke et al., 2006). This allows a better estimate of the dust mass and in reality, oxygen is always associated with these elements. We recognize that some Fe may be as FeO but XRF does not distinguish Fe(II) or Fe(III). We added a sentence to explain why we used Fe2O3 and also clarify the potential presence of FeO that we did not consider: Lines 173-175: The total mass on filter was calculated as the sum of the mass of the oxides of the major crustal elements reported in Table 1. Fe is assumed to be as Fe2O3. We recognize that Fe(II) and Fe(III) can be found in the mineral phases (e.g., magnetite, augite) and in the amorphous glass, but the Fe(II)/Fe(III) ratio is not known.

Comment 9: 357-359: The photochemical activity is commonly described for rutile. But this is not identiïñĄed by XRD, instead titanomagnetite is found. Also, the glass phase could contain considerable amounts of Ti, as the titanomagnetite contents doesn't seem to explain the total TiO2 content. Therefore, the conclusion here doesn't appear to be sound.

Response: (same response as to the second comment of referee 1) This paragraph

has been modified according to the referee's comments: TiO2 catalyses heterogeneous photochemical reactions of atmospheric trace gases including SO2, NO2, VOC and O3, and contributes to the chemical balance of the atmosphere (Chen et al., 2012). In North African and Asian dust, TiO2 is around 1% (e.g., Formenti et al., 2014; Jeong, 2008; Shi et al., 2011). In Icelandic dust, the element oxide concentration of Ti is relatively high 2-5.5%, although Ti can be not just as TiO2 minerals (anatase and rutile). Ti may be present in magnetite and aluminosilicate minerals (e.g., augite) or in the amorphous glass.

Comment 10: 506-510: The conclusions refer to magnetite, but mainly titanomagnetite was identified. Is there anything known about the optical (and also Fe dissolution) properties of the latter?

Response: Titanomagnetite (Fe$_{3-x}$Ti$_x$O$_4$) forms a complete solid solution series between the end-members magnetite (Fe$_3$O$_4$) and ulvöspinel (Fe$_2$TiO$_4$). Hettiarachchi et al. (2019) observed that there is a strong correlation between the Fe solubility and the Ti/Fe ratio, which suggests that the presence of Ti in magnetite can enhance its solubility. Currently, there is limited knowledge of the optical properties of titanomagnetite minerals. Both magnetite and ulvöspinel strongly absorbs light throughout the UV-Vis region, although they may have different spectral features (e.g., the absorption peak in ulvöspinel is shifted from 300 nm to 500 nm) (Strens and Wood, 1979). The spectral feature of minerals of the titanomagnetite series may also depend on the Ti/Fe ratio.

Corrections:

72: Check the spellings of Möller/Moller/Moeller. They have the same name (Möller) 85: Check the references. E.g., Urupina is not in the list. 93: Dust source areas? 167-170: That can be removed, as creation of deïňĄned standards is not topic.

Response: All the corrections have been applied in the text. âĂČ References

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