

Interactive comment on “Composition and mixing state of atmospheric aerosols determined by electron microscopy: method development and application to aged Saharan dust deposition in the Caribbean boundary layer” by Konrad Kandler et al.

Anonymous Referee #2

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General comments:

This manuscript presents new methods for accurately determining composition and mixing states of individual coarse aerosol particles by an automated SEM-EDX, and their application on the aged Saharan dust samples collected in the Caribbean boundary layer. Traditionally, individual particle analysis suffered from uncertainties related to poor counting statistics. There has been a significant gap between the ambient mass

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size distribution and such qualitative information based on individual particle analysis. The authors however, succeeded to analyze large number of particles by the use of a novel automated SEM-EDX, and to provide a much more comprehensive and quantitative view on the mixing states of dust as a function of particle size. Sampling and data analysis were done very carefully by taking into account many potential sources of errors and uncertainties (e.g. quantification of elements, estimation of dust mass, sampling artifacts, counting statistics) and they are well defined and characterized in the manuscript. I therefore believe the manuscript deserves certain credit and can be a good contribution to ACP. However, such thorough and detailed verification of the methods in turn made the manuscript rather lengthy (especially the method section) and not easy for the readers to digest its major findings. It requires an extensive restructuring, and there are also some concerns on the assumptions made and interpretation of the results. The paper may be recommended for publication after these concerns are properly addressed. Specific comments are listed below:

Specific comments:

Lines 17-19: Please rephrase “Techniques were developed to conclude from collected aerosol on atmospheric concentrations and aerosol mixing state, and different models were compared.”

Line 51: “Data basis is still limited” can be elaborated to make this study stand out more from previous studies.

Line 56: methodological?

Lines 68-623: While introduction section is made up of only 3 paragraphs, method section accounts for the majority of the manuscript and the overall structure appears rather unbalanced. Many details, equations and figures in the method section can be moved to supplementary information (SI). The explanation in the text can be significantly shortened by simply referring to corresponding sections in the SI.

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Line 69: Sampling time and duration for three different samplers are not well explained. How do they coincide? I imagine deposition sampler requires longer time.

Line 147: As a result,

Lines 175-178: Validity of estimating volume equivalent diameter (in section 2.3) based only on 2-dimensional projected area and perimeter is questionable. It may work rather well for dry and solid particles such as pure silicates, but if particles were internally mixed with soluble materials and sampled at high relative humidity conditions (which might often be the case at Ragged Point), flattening of deliquesced particles on the substrate may become a source of significant sizing bias. Some people employ tilting of sample stages or apply shadowing to measure the height of the particles under SEM analysis.

Line 185: achieved instead of reached?

Lines 196-197: How exactly does a smaller accelerating voltage (12.5 kV) ease the particle morphology problem? Please explain.

Lines 212-213: "...which not only includes particle but also the substrate."

Lines 213-214: Please rephrase "they do only indirectly represent an amount of matter with respect to the particle."

Lines 217-218: "...while the remaining uncertainty originates mainly from the particle to particle variation."

Lines 222-223: why is the case for 20 kV is shown instead of 12.5 kV?

Line 255: "...separately is an important task."

Line 328: here may suffer?

Lines 349-350: "chemically aggressive environments" is too vague. Please elaborate. Representing bio-available iron by spherical surface area and metal oxide mass fraction

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alone may be misleading and needs further explanation about its limitations, since Fe dissolution is also highly dependent e.g. on pH and presence of inorganic and organic ligands (which cannot be addressed by the current analytical approach).

Line 659: As a result,

Line 757: e.g.

Line 778: "...while a strict disambiguation can't be done for elements also found in sea salt."

Line 779: "most likely derived only from dust"

Line 790: Western Africa

Line 894: considerably higher

Line 896-908: With regard to the change in dust behavior due to internal mixing, I generally have no objection about the main conclusion that the mixing of dust with sea-salt and sulfate would significantly affect its deposition velocity as stated in the preceding paragraph. I also admit that the conclusion is well supported by the solid results shown in this study. In contrast, the whole idea about enhanced ice-nucleation efficiency of dust through internal mixing needs more careful discussion and is not supported by sufficient results. For example, some studies report deactivation of ice nuclei due to atmospherically relevant coating (e.g. Cziczo et al., Environmental Research letters, 2009), and this deactivation by coating may be more pronounced especially for deposition mode ice nucleation. This impact of coating on different freezing modes might need to be explained clearly in the text not to confuse the readers. Also, the heterogeneous ice freezing temperatures of dust can decrease with increasing concentration of different solutes (e.g. Zobrist et al., J. Phys. Chem. A, 2008) in immersion freezing. There may be a regime where cloud droplets are not dilute enough such that freezing temperatures of droplets activated upon sea-salt / dust mixture can be significantly decreased (Iwata and Matsuki, ACP, 2018). There could be several competing effects

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of coating on dust ice nucleation efficiency and this may not act identically for different freezing modes. Besides, as authors pointed out themselves (in line 890), mixed particles with a smaller contribution of hygroscopic material, which remain undetected by the current analytical approach, may be present. Droplet growth and activation kinetics may behave differently at sub- and super-saturated conditions and such seemingly uncoated dust may as well be activated as cloud droplets under higher supersaturation. This subject may need a whole new paper to be discussed. Since there are not much results to support the proposed hypothesis, this whole section about the proposed enhancement of dust ice nucleation efficiency may even be omitted from the current manuscript.

Fig. 18: In this context, isn't the annotation for the third figure from the top supposed to be "sea-salt/silicate mixtures" and "sulfate / dust mixtures"?

Line 1468: "size class is shown in conjunction with. . ."

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