

Interactive comment on “Exploring the variability of aerosol particle composition in the Arctic: a study from the springtime ACCACIA campaign” by G. Young et al.

Anonymous Referee #2

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General Comments

This study analyzed the size distributions and element compositions of samples collected by aircraft during the springtime segment of the Aerosol Cloud Coupling and Climate Interactions in the Arctic campaign (ACCACIA). The study is important because it leads toward a better understanding of the composition of particles directly below and above clouds in the Arctic. The types of particles studied here could have served as cloud condensation nuclei or ice nucleating particles in the vicinity of Svalbard, Norway, and therefore, may lead toward a better understanding of the effect of clouds on the Arctic climate. The paper cites existing literature extensively, which nor-

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mally is most helpful. However, here the literature could have been presented more concisely, and thus, for this reason alone the paper could have been shortened.

The paper presents a substantial amount of information that was reported previously in the literature, and thus, need not be reported here. For example, Section 2.3 discusses extensively the process of analyzing particle populations with energy-dispersive x-ray spectroscopy associated with SEM. Particle population analysis by SEM has been well established for decades, including normalizing the composition by weight percent, which is the only plausible way to report composition if particle standards are impractical. In another example where the lack of a concise explanation causes some confusion, the authors indicate in one place that carbon and oxygen were measured, but later indicate that carbon and oxygen were not quantified. More about this below under Specific Comments.

In reporting of results and the follow-up discussion, some of the interpretations are questionable or lack the appropriate emphasis. For example, I do not see where one can draw convincing conclusions from Figure 5 about differences in the complement of particles classes between smaller particles (<0.5 μm) and larger particles (>0.5 μm). As the authors admit, the compositional variability is great among the samples from the different aircraft flights. The between-sample variability in Fig. 5 overwhelms any size-dependent trend. Regarding appropriate interpretive emphases, the authors make a number of definitive claims of the data showing a “clear” effect where the data are more nuanced. I recommend that the authors be more careful in interpreting their data. Specific examples are presented below.

Overall however, I find the paper informative because the authors do manage to return at the end of the paper to their main objective. That is, they discuss rather well (with appropriate caveats) how the size-segregated compositional analysis here relates to CCN, INPs and cloud microphysics.

Specific Comments

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Introduction

29407 Section 1.1 line 22

Nuclepore is a trade name. It would be good to indicate the source (i.e, manufacturer) of the filters.

Methodology

29408 Section 2.1 paragraph 2

There is extensive particle-size overlap among the particle size distribution techniques used: PCASP, CAS-DPOL, and CDP. This suggests that for the overlap regions these probe techniques could have been compared. However, this was not done.

Section 2.3

The paper describes the use of an ESEM with EDS for analyzing the various polycarbonate filter samples. The ESEM is used in the high-vacuum mode, so it functions here as a conventional SEM with EDS. Since the instrument is not used as an ESEM, i.e., at low vacuum with a water vapor atmosphere, it should be indicated in this section that the instrument is essentially a conventional SEM to avoid confusing readers unfamiliar with an ESEM. All later mentions of ESEM in the paper should be changed to SEM.

29410 lines 19-21

The paper explains at length how particle are analyzed by SEM, and as mentioned above, much of this is already in the literature. There is, however, one significant gap: the software procedure used to perform the particle population analysis in the SEM should be better explained. It is stated that the electron beam is controlled by the EDS system to provide automated analysis of the sample, i.e., the analysis of the particle population on a filter. This implies that the X-ray signal is used to detect the presence of a particle and determine where in the particle spectra are to be taken. I know of no commercial software, EDAX Genesis included, that does this. Rather, software uses

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the backscatter electron or secondary electron signal to detect a particle. Typically, software decides where to point the beam within the particle for X-ray collection by assessing the shape of the particle and then judging where the center of the particle is. The paper fails to indicate whether the backscatter or secondary electron signal was used and whether the beam was held stationary or rastered within the particle. These issues should be made explicit in the Methodology.

29411 lines 6-7

It is indicated that carbon and oxygen are included in the analysis. However, these elements would be highly problematic because X-rays from the polycarbonate substrate would certainly penetrate the particles. The authors do mention this problem, and two paragraphs later they state that carbon and oxygen were not included. It would be clearer and more concise if the authors simply stated that carbon and oxygen were not quantified. Later the authors indicate that the presence of carbon and oxygen in an X-ray spectrum containing no other elements provided evidence that the particles were carbonaceous. Here, we are to assume that carbon and oxygen in a spectrum were used qualitatively, not quantitatively.

29411 paragraph 2

This paragraph focuses on an analysis of a blank. More information should be provided about the nature of the blanks. For example, how many blanks were used? Were they field blanks in that they were somehow exposed in the aircraft, or were they simply lab blanks taken out of a box prior to the SEM analysis? Field blanks are much preferred in this type of study.

29413 Section 2.4 and Table 4

The omission of quantitative carbon and oxygen measurement and the identification of carbonaceous particles based on the x-ray spectrum exhibiting qualitatively only carbon and oxygen has a significant drawback. Certainly, the authors were correct

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to avoid quantifying these elements. However, mixed-phase aged particles of carbon (organic or soot) plus mineral dust could not be classified, not to mention carbonate minerals alone. The authors should discuss this drawback and possible solutions.

The classification scheme presented in Table 4 only indicates qualitatively how particles were classified. The actual scheme had consist of numeric boundaries, i.e., weight percent boundaries. What do the following mean: “significant Na and Cl”, “major fractions of Na, Cl, S”, “mixtures primarily containing Si and Al”, etc? It is important to report the quantitative scheme so other researchers can utilize the same scheme if desired.

29418 lines 4-8

Why is it implied that particles are well mixed if they are classified as other, i.e., not within the classification scheme?

Also, the following statement is problematic: “. . . the automated scan will not catalogue the spatial dependencies and instead computes a mean spectrum for presented particle surface area.” It is important to use precise wording. Scanning in automated SEM allows for the detection of a particle from the backscattered electron or secondary electron signal. Typically, the acquired spectrum is not a mean but rather the result of the electron beam held stationary on the particle for a duration after the particle center is determined. To clarify, the authors should state that automated SEM for particle analysis does not acquire an element spatial map of each particle.

Results

29420 lines 9-15

I don't think it is correct to say that the agreement between the SEM data and the probe data is clearly dependent on whether or not the cloud was sampled. There appears to be some dependence, but I would say that the out-of-cloud B765 case exhibits less agreement between the SEM and probe data than for the B761 case

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which had exposure to the cloud. Here, the authors should be more careful in their cause-and-effect assertion.

What is more interesting and obvious is the lack of agreement between the SEM and probe data in most cases (the exception perhaps is B768) for particles < 1 μm . Presumably, the PCASP can assess sizes down to 0.1 μm while the SEM analysis can assess sizes down to 0.13 μm (Table 3). We are left hanging on this issue until the Discussion section. It would have been helpful if the authors acknowledged the obvious here in Results and said something like: “more about this in the Discussion.”

29420 Section 3.3

I am not sure what is meant by an “element index” in the first paragraph. If one simply takes the composition data normalized to weight percent in the analysis software, then the effect from the filter is not a problem.

29421 and Figures 5-8

The classification data presented in Figure 5 are far less informative than data presented in Figs. 6 and 8. The only reasonable conclusion drawn from Fig. 5 is that distribution of particle classes between flights is highly variable. I do not see how the mixed chlorides and metallic classes are independent of size. I cannot agree that sulphates, carbonaceous, and biomass tracers are strongly detected in the smaller particles. There is too much between-flight variation. I would caution the authors against reading too much into Fig. 5. In fact, the authors may not want to use Fig. 5 at all.

Figure 6 shows a clearer distinction between particles sizes based on particle classes. However, this appears to be due to the authors selecting particles sizes where there was agreement between the SEM size data and the probe data.

Figure 7 shows only a few “clear” distinctions: in particular, the elevated K/Al, Ca/Al, and Fe/Si levels for the B768 case. Again, I would caution the authors against making strong statements such as there being a “clear” peak in the Si/Al data for the B764

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case. Yes, it is the highest mean, but the B765 mean is very close.

Figure 8 is perhaps the most relevant of all in this paper because of the positional importance of bands CCN and INP (below vs. above) with respect to the cloud.

Discussion

29425 Case B768

I do not see how the authors can make the claim that Fig. 4 shows a much higher particle loading for the B768 case. The probe data B768 data are about comparable to the B765 data and perhaps less overall than the B761 data.

29428 Section 4.3

I do not see how one can assess with confidence the degree of internal mixing from the variability in the mean composition fractions in Fig. S1. Internal mixing suggests that particles have spatially-separated phases such as for the particle in Fig. 2. (I would disagree that this is a “well-mixed” particle!) In this paper, it seems that internal mixing is determined by the number of elements detected in the particles. As many minerals are compositionally complex, a mineral particle may be compositionally complex but with phases that are not spatially separated, and thus, the particle cannot be considered internally mixed.

Conclusions

29431 lines 1-5

As stated above, conclusions drawn from Fig. 5 are not convincing. I do not see where one can say that carbonaceous particles and sulphates are prevalent in the smaller particles – more present, yes, but not prevalent.

Interactive comment on Atmos. Chem. Phys. Discuss., 15, 29403, 2015.

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