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Atmospheric Chemistry and Physics
Discussions

Interactive comment on "Sub 500 nm refractory carbonaceous particles in the polar stratosphere" *by* Katharina Schütze et al.

Katharina Schütze et al.

schuetze@geo.tu-darmstadt.de

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We gratefully acknowledge the suggestions of the anonymous Referee II and included them to the revised version of the paper. We believe that the changes considerably helped to improve the quality of the manuscript.

Anonymous Referee #2

The above manuscript deals with electron microscopy (TEM, SEM) analysis of stratospheric particles sampled mainly in the Arctic polar vortex. As such measurements are rare, the presentation of the measured data is well suited for ACP, even if the results are not totally conclusive. However, there are some points, which should be improved before publication, some work, but feasible.

General remarks:

The first thing, which immediately leaped out at me when reading the abstract, was the big difference between the time of sampling and the time of publication. The samples were taken in 2000, now we have 2017. When was the analysis done? If it was in recent years, how where the samples stored in-between? How might the particles have changed during this long storage time? If the analysis was performed shortly after sampling, why did the publication take so long? The authors have to address this issue in a new paragraph.

The samples were collected in 2000, analysis started late in 2013. The samples were stored in a desiccator and we found them worth to be analyzed since data on stratospheric particles are sparse. As we also investigated blank samples, which were packed in the same sampling device (MACS), and stored in the same way as the real samples, we can exclude contamination from vapors of the plastic box or other possible artifacts related to storage. This issue is accordingly addressed in the last paragraph of chapter 2.1 in the paper: "The stratospheric particle samples (deposited on TEM grids) taken within the polar vortex, were packed into single plastic boxes and stored in a desiccator prior to analysis, starting in 2014. Based on the investigation of blank samples, contamination of the samples during the time of storage (e.g. by vapours from the plastic boxes) can be excluded. Furthermore, a change in particle morphology and nanostructure is not expected, since the particles found are either amorphous or show very little ordering. This conclusion is based on the fact that graphitization of carbonaceous material is an irreversible process (Diessel et al., 1978; Itaya, 1981; Pesquera and Velasco, 1988). Anyhow, it should be kept in mind that other parameters (chemical composition, mixing state) may be changed to a variable extent by aging."

Secondly, concerning the samples, section 2.2. There are 11 samples, OK, but I got confused how many particles where analyzed with which method. Were some particles analyzed with both methods? Moreover, on page 4, line 21 you even mention STEM, which is not mentioned somewhere else. Was this an additional method? Then it should be listed in the abstract as well. To make it easier for the reader to understand what you did and not to put too much workload on you, I suggest to include another table, where the reader gets an overview how many particles where analyzed with which method (and detector).

We agree that the reader gets confused about how many particles were analyzed with which method. Therefore we added a new table 2 at the beginning of chapter 2.2. STEM is an additional tool in TEM with the opportunity to get high-resolution information on the element distribution within nanoparticles. STEM images are shown in figure 6 and were mentioned in the discussion paper on p.7 l. 24. We also added the 4 particles investigated by STEM and the 23 particles where the nanostructure was investigated to the total number of investigated particles (4202) in the introduction as well as chapter 2.2.

Another point, there are many statements in the manuscript, which are not specific enough. This occurs quite often, when citing the literature (which might not be the fault of the present authors, maybe the original authors were not specific enough). I tried to list some examples of that below. Please have a look throughout the manuscript and improve the text. Finally, there are another two important issues (measurement artifacts and particle aging), which are explained in the following section in detail. Specific remarks: Abstract: - p. 1, l.15: "... approximately 28-82% of the particles are refractory carbonaceous ..." This statement is not very specific. You can nearly find all fractions of refractory carbonaceous particles, well OK, everything is possible, not very useful, but how likely is that? Moreover, isn't the range much smaller, 52-82% (Fig. 3), considering that sample G seems to be a special one?

After studying the reviews of both reviewers, we figured out that we are introducing large errors especially by stating relative numbers of refractory and volatile material. We probably highly underscore volatile particles because of a) losses during sampling (e.g. bounce off), b) losses under the high vacuum conditions under the electron microscope and c) errors in counting because of the impaction of more than one particle

on the same spot. Therefore we decided to remove figure 3 from the manuscript and thus the relative occurrence of refractory and volatile particles.

- p. 1 1. 17: "20-830 nm" this contradicts the manuscript title, i.e. the "500 nm

We agree and changed the title to "Sub-micrometer refractory carbonaceous particles in the polar stratosphere"

- p. 1 1. 21: The ratios to C: It would help the reads imagination if you would provide the ratios as fraction, i.e. instead of for instance "0.001" use "1/1000". Same for the detection limits in section 2.2. As the first place is the abstract, showing your major findings, you should also asses the meaning of these numbers, are they common or rather rare, what do they indicate, etc.

We do not agree and prefer "0.001" for clarity reasons. The numbers are given for the reader as a summary of the findings. We did this to give the reader as many information on the particles as possible, as we faced that in the current literature necessary information on particles is often missing in order to be able to compare data. Based on that fact, publications with information on element ratios are rare in literature. This also counts for descriptions of particles for specific sources. As this information is missing in literature, it is not possible to compare the data or give information what the numbers exactly indicate.

- p. 2 1. 25: Ebert et al. 2016, from the same group, what are the similarities, what are the differences between this paper and the current manuscript? It should be possible to compare the results.

The results from Ebert et al. 2016 are totally different to the ones from this study, as those authors found, besides the volatile particle group, eight different particle groups. The differences of Ebert et al. (and other authors) to the findings of the current study are discussed in the second last paragraph of section 4.1: "In the present study, only carbonaceous particles and sulfates were observed similar to previous findings

(Pueschel et al., 1992; Blake and Kato, 1995; Strawa et al., 1999; Nguyen et al., 2008). There are, however, several previous publications which describe the presence of a variety of other refractory particle groups in addition to carbonaceous particles. These additional particle groups include metallic particles (Chuan and Woods, 1984; Sheridan et al., 1994; Chen et al., 1998; Baumgardner et al., 2004; Ebert et al., 2016), meteoritic particles (Murphy et al., 1998, 2007, 2013; Renard et al., 2008, Ebert et al., 2016), silicates (Testa et al., 1990; Ebert et al., 2016), crustal-type particles (Sheridan et al., 1994; Chen et al., 1998), as well as Ca-bearing particles (Della Corte et al., 2013; Ebert et al., 2016)."

- p. 3 1. 4: redistribution vs. sedimentation: Currently your statement reads like an exclusive "or", but both processes can happen to a specific trace gas, it can be redistributed and be removed by sedimentation, or?

We agree, and changed the paragraph accordingly.

- p. 3 1. 6: In this paragraph, you list a bunch of sources for stratospheric refractory particles. However, the reader does not know, which one is the more important (e.g. with respect to mass or frequency of occurrence). Could you please provide the reader with such an additional information.

In the paragraph mentioned, we list the most probable sources for refractory stratospheric particles. Unfortunately no publications exist on the frequency of contribution from different sources to the refractory particle load. This is most probably the case because most of the sources do not occur continuously but are rather irregular features. Therefore we added an additional sentence to provide the reader with this information: "As the frequency of particle emissions from the listed sources is highly variable, the individual contribution of the various sources is, in general, not quantifiable"

- p. 4 1. 2: It is stated that the vortex was stable between mid-January and mid-March. This was exactly the time of sampling and you should mention here that the presented data are from this period.

Accordingly the sentence was changed to "During the period of airborne measurement operations, from mid-January on, the vortex evolved to be continuous and stable until mid-March (Greenblatt et al., 2002)."

- p. 4 1. 11: the selection criteria "substrate area covered by particles", what does it mean? I′m not an electron microscopy specialist.

For analysis by electron microscopy it is important to achieve a suitable particle load on the substrates. Particle overloading means too many particles in one certain area, which makes it impossible to identify and characterize individual particles. Thus, the mixing state cannot be doubtlessly identified and it is not possible to identify individual particles. Too little particles in a certain area of the impaction spot have too little material to achieve a representative number of analyzed particles.

- p. 4 sect. 2.2: The two silicon-EDX detectors from Oxford, are they the same? Once Oxfordshire, once Wiesbaden? Isn′t it the same company?

Yes, both EDX-detectors are the same! Therefore we changed the sentence to: "The instrument is equipped with the same type of EDX-detector as the Philips CM20 instrument."

- p. 5 1. 10: Not being an electron microscopy specialist: what would you expect the scattered electrons do? Hit the housing and generate x-ray emissions there? Please clarify.

According to your statement we included the following sentence for clarity: "This could lead to the detection of chemical elements in the vacuum chamber's housing material."

- p. 5 1. 17: "small but systematic differences". Please specify what "small" means, e.g. give a percentage range. Same for line 21.

In order to show what the differences between the measurements with the differences are, we introduced a new table for the electronic supplement; S2. In this table the median values for element ratios are shown both for SEM and TEM.

- p. 6 l. 15: “all particles” in the world? The stratosphere? On a sample? Which diameter does the spot have?

The sentence was accordingly changed to: “All collected particles are located within a characteristic impaction spot having a diameter of $\sim$350 μm.”

- p. 6 l. 25: For me, sample G seems to be special. Did you check how the sampling conditions of sample G are compared to the other samples?

We checked the conditions of sample G and also found an error in Table 1 which we changed (wrong order of PV-values). Thus we figured out, that sample G is from a multiple level flight and shows the lowest potential vorticity (18.2 PVU) and the second highest N2O value (209 ppbv). Furthermore sample G was one of the samples collected in the lowest altitudes (17.4 km) and shows, thus, a comparably high pressure and low potential temperature. Based on those facts we changed the values in table 1 and also added values for N2O.

- p. 7 l. 1: In Fig 4, sample E and F show a very different distribution width. Did you check for reasons?

We do not have any answer to this question since we do not have any idea what that difference in distribution width between the samples is due to.

- p. 7 l. 7: The minor components you have found (Fig. 5): From the literature (e.g., Murphy et al., AS&T, 2004; Martinsson et al., AMT, 2014) it is well known that ice crystals hitting the aerosol inlet can remove inlet material, bring it into the air and thus can generate artificial particle signals. Fe and Ni are known for this. Did you check the correlation between the occurrence of these elements with the ice crystal number concentration or the sampling time spent in ice clouds? This is important and must be addressed in order to trust your data.

The elements Fe, Cr and Ni are only abundant as minor elements in carbonaceous particles. Furthermore, STEM images reveal that those particles do not occur as in-

clusions in the particles but as small traces widely distributed within the particles. In contrast, particles both described by Murphy et al., 2004 and Martinsson et al., 2014 are solely consisting of all or some of the elements Fe, Cr or Ni. Thus we regard our particles as totally different as the ones found by those authors. Abrasion particles are easily identifiable with electron microscopy techniques by their morphology (sharp edges), size and chemical composition. Based on our longtime experience with tropospheric particles we can certainly exclude the carbonaceous particles to be abrasion products. In order to make this fact clear for the reader, we changed the paragraph to: “Besides C, the refractory carbonaceous particles always contain O and Si (Figures 2, 4 and 5), and in most cases also S. The element Si may at least partly be an artifact of the substrate. The S X-ray peak in EDX-spectra originates either from sulfates internally mixed with the carbonaceous particles or from stray radiation. Please note that the heights of the individual peaks in figure 2 are not proportional to the element concentrations, but give a rough estimate of the element abundance. The elements Cr, Fe, and Ni are often found as minor component (Figure 4). These three elements exclusively occur within the carbonaceous matrix, and are not abrasion products from ice particles hitting the aerosol inlet as the metallic particles described by Murphy et al. (2004) and Martinsson et al. (2014). Furthermore, none of the samples was collected during the existence of ice particles which could potentially remove material from the impactors’ inlet. During collection of samples A, B, E and G, polar stratospheric cloud particles (PSC) containing oxides of nitrogen, NOy, were abundant. As we found the refractory carbonaceous particles in all samples independent of the occurrence of NOy, they are not artifacts from the removal of material from the inlet system.“

- p. 7 l. 24: For how many particles was this element distribution imagine done? Fig. 6 shows just one. Is there any statistics on the results of this analysis?

Element distribution imaging and spot measurements were only conducted on four particles as this is a very time consuming approach. We did this in order to get to know if STEM shows any heterogeneous inclusions which we were not able to see either with SEM (in backscattered imaging) or TEM. This little investigation shows, that the minor elements are homogeneously distributed within the particles, e.g. the particles do NOT contain elements heterogeneously distributed.

- p. 7 1. 25: I do not know how the element distribution images work, hence I do not know what "measuring several" (how many?) "points on the particles" means. Please explain this more in detail.

In element distribution images, the chemical composition of a single pixel within the image is reported. The images shown in fFig. 5 do all have a pixel size of 256x256. We changed the paragraph to: "The spatial distribution of minor elements within the carbonaceous particles was investigated by element distribution images in STEM (Figure 5) with a 256x256 pixel resolution as well as by measuring several points on the same particle. With both approaches it is possible to obtain highly resolved information on the spatial distribution of elements within a nanometer-scale particle. C is the most abundant element and is found in the whole particle."

- p. 7 1. 31: Why did you generate these four groups? If I did not overlook it, they are not used afterwards.

As we were aiming to characterize the refractory carbonaceous particles in as many details as possible, we found it useful to show the occurrence of the minor elements in the different samples. That some particles contain all of the minor elements Cr, Fe and Ni, but others do not contain any of them or just some is also shown in EDX-spectra in figure 2. In order to show the abundance of particles with or without minor elements, we decided to show this also in Table 2.

- p. 9 1. 22: The differences between your study and the results in Nguyen et al., 2008 is likely due to the different atmospheric measurement regions and different measurement altitudes. You should mention that, otherwise the reader might take the Nguyen reference as a contradiction to your findings, which is, in my point of view, not the case.

We agree that there are similarities to the results of Nguyen et al., 2008. Therefore we changed the paragraph to: "Mixed carbon-sulfur particles were observed by Nguyen et al. (2008) (diameter ≤ 1 μm) at 10 km altitude between 50°N and 30°S. These particles were assumed to have formed from condensed organic matter. The differences between these particles and those found in the current study might result from differences in sampling altitudes and regions. Therefore we cannot totally exclude the particles to be different, taking into account that the particles might have evolved from condensed organic matter. However, we do not know if secondary organic particles become refractory as a result of atmospheric processes."

- p. 10 1. 11: Pyro-convection is defined as fire-started or fire-added convection, hence the definition given by you is incomplete.

We have changed the sentence to "This material was thought to be injected into the stratosphere by the pyro-convective effect (i.e., fire-started or fire added convection)."

- p. 11 aircraft exhaust section: The Mazaheri et al. reference here, and later on also the Tumolva et al. and Torvela et al. references in the wood burning section, here you compare freshly emitted particle properties to your particles, which are, because they were measured in the polar vortex, likely more than one year old. This comparison can only fail, the particles aged and strongly changed. I miss this time effect in all potential source paragraphs, but this point is important and must be considered in the discussion section.

We agree and added the following paragraph before the "aircraft exhaust" section which regards all following paragraphs: "Most particle groups discussed in the following were collected close to their emission source. We are aware of the fact, that particles collected in the polar stratosphere may in principle change their properties during their atmospheric lifetime. However, ordering of carbonaceous material is an irreversible process leading always to a higher degree of ordering (Diessel et al., 1978; Itaya, 1981; Pesquera and Velasco, 1988). As most of the particles analyzed show no or only very little ordering, it is assumed that the particles did not change their nanostructure during their atmospheric lifetime. On the other hand, several electron microscopy studies describe soot particles in the stratosphere (Pueschel et al., 1992, 1997; Sheridan et al., 1994; Strawa et al., 1999; Ebert et al., 2016). Thus, it can be expected that soot particles - once injected into the stratosphere – do not change their typical nanostructure under stratospheric conditions."

- p. 11 1. 26: Consider to add "(dominant meteorite fraction)" or something similar after "chondrites", in order to explain what this thing is.

We have changed the sentence to: "Carbonaceous material is observed in chondrites (dominant meteorite fraction) as well as in interplanetary dust particles (IDPs)."

- p. 15 1. 1: The summary is too short. You did a lot of work, please expand the summary.

We changed the summary to: "The major finding of the present study is that the refractory component consists of carbonaceous particles only, with a number mixing ratio of 1.1 (mg air)-1 (median for all samples). Most carbonaceous particles are not internally mixed with or coated by sulfates. The particles were sampled in air having low abundance of N2O and therefore long residence times in the stratosphere. Thus, one would expect them to be covered with condensed sulfuric acid resulting from the oxidation of COS (Wilson et al., 2008). The reason for this discrepancy is not known. As major elements only C and O were detected. Most of the carbonaceous particles show small and variable amounts of Fe, Cr and Ni. These minor elements are distributed in the carbonaceous matrix, i.e., they do not occur as heterogeneous inclusions. Most carbonaceous particles are completely amorphous. The exact source of the refractory carbonaceous particles remains unclear and can only be confined by exclusion. Based on the investigated physical properties and chemical composition of the particles, aircraft exhaust, volcanic emissions and biomass burning can be certainly excluded as source. The same is true for the even more unlikely sources wood burning, coal burn-

ing, diesel engines and ship emissions. It is expected that exhaust of rockets powered by kerosene or other hydrocarbons emit soot, but due to the lack of available electron microscopy studies of these emissions, rocket exhaust cannot be excluded as a possible source of the refractory carbonaceous particles found. Carbonaceous material from IDPs and extraterrestrial particles, likely originating from meteoric ablation and fragmentation remain as the most probable source for the particles encountered in the current study." We also deleted the last sentence as we have changed our conclusions based on the remarks of both reviewers and the interactive comment of Alexander D. James.

Technical corrections:

- p. 1 1. 29: Please remove the empty line, the last sentence of the abstract belongs to the upstream paragraph and should not be separated. Changed accordingly

- p. 2 l. 3: "sulfur" is an "element", not a "component". Changed accordingly

- p. 2 1. 13: which "groups" where identified? "Particle" or "morphology" or . . .

We have changed the sentence to: "However, due to the lack of instrumentation, the chemistry of the particles could not be investigated. Refractory particles with diameters >1 μm were studied in more detail by Zolensky and Mackinnon (1985), and several particle groups were distinguished. . ."

- p. 2 1. 15: "a large refractory particle load", what does this mean? With respect to particle mass or particle number or just fraction of particles containing refractory material?

We have changed the sentence to: "In contrast to prior findings, a large number of refractory stratospheric particles was recognized by Zolensky et al. (1989)"

- p. 2 1. 20: "widely distributed", what does this mean? All over the globe? Or at all altitudes (which ones?) in the area of investigation (which was?)?

We have changed the sentence to: “Carbonaceous aerosol was found to contribute to the aerosol population at all latitudes in the stratosphere and interplanetary dust was significantly abundant above 30 km for particles $\geq$ 0.35 μm (Renard et al., 2008).”

- p. 2 1. 22: I′m not a native speaker, but shouldn′t it be “Earth′s”?

We have changed it accordingly

- p. 2 1. 31: “condensation of saturated gases”, it is not necessary to provide seven (!) references for this textbook process. As it disturbs reading the paper, you should reduce the number.

We agree and deleted four of the references!

- p. 3 1. 25: Please insert a comma after “impactor”.

Comma inserted.

- p. 3 1. 26: Please remove the “The” before “MACS”.

“The” removed.

- p. 3 1. 32: “It was weaker . . .” What is “it”? The “Arctic winter”? But then the sentence does not make sense.

We have changed the sentence to “The vortex was weaker than the early winter polar vortices of the previous years.”

- p. 4 1. 4: Please use “Θ” instead of “PT”.

Changed accordingly

- p. 4 1. 20: Please move “software” before the brackets.

Changed accordingly

- p. 4 sect. 2.2: Please use “EDX” instead of “energy-dispersive X-ray” throughoutly, after you defined it once.

Changed accordingly

- p. 6 1. 29: The whole statistical analysis section reads like a bullet point list. Please make it more a coherent text or a real bullet point list, with an introductory text.

We have changed the section to “Censored boxplots show data taking into account the fraction of values below detection limit. Lower and upper quartiles appear as a box, minimum and maximum values as whiskers. The differences in element ratios between samples collected inside and outside the vortex were tested with the generalized Wilcoxon test (Helsel, 2012) applying a significance-level of 5%. Furthermore, the differences in size, projected area diameter and element ratios between the various samples were tested with the Kruskal-Wallis rank sum test (uncensored data) and the generalized Wilcoxon test (censored data). In all individual tests, a significance level of 5 % was applied. The detection limits for EDX data were calculated from counting statistics (background counts plus three times standard deviation of background counts). All statistical calculations were performed with R (version 3.3.0; R Core Team, 2016) and using the contributed package NADA (version 1.5-6; Lee, 2013).”

- p. 6 1. 7: Please remove “applying a significance level of 5%”, this is redundant, as it is mentioned in the last sentence of this paragraph.

Accordingly removed

- p. 6 1. 15: Please move the comma after “(Figure 1)”.

Changed accordingly

- p. 7 1. 1: Please use “indicated” instead of “shown”, you do not show real particle size distributions, e.g. dN/dlogDp.

Changed accordingly

- p. 7 1. 6: Please move “besides C” to the beginning of the sentence.

Changed accordingly

- p. 7 1. 25: Please replace “contained in the whole” with “found everywhere in”.

Changed to “. . .and is found in the whole particle”

- p. 8 1. 18: Please replace “The samples” with “All samples”.

Changed accordingly

- p. 10 1. 27: Please replace “emissions” with “eruptions”.

Changed accordingly

- p. 11 1. 15: A space is missing before “The”.

Changed accordingly

- p. 11 1. 16: Please replace “at” with “in”.

Changed accordingly

- p. 12 1. 27: “comprised . . . to” sounds strange, better use “contribute . . .to” or something similar.

Changed accordingly

- Fig. 2: Please specify Kα and Kβ in the figure caption. What does “all particles” mean? In the stratosphere or all sample or all refractory? Is the peak height/area linearly representative for the number of atoms? This should be mentioned somewhere in the text.

We did the specifications as suggested. The figure caption now reads like: “Figure 2: TEM bright field image (a) of a typical refractory carbonaceous particle from sample H (19.1 km altitude). The image is representative for all refractory carbonaceous particles. The morphology is not depending on chemical composition, size, morphology or nanostructure. Energy-dispersive X-ray spectra of (b) a typical refractory carbonaceous particle with Fe, Cr and Ni, (c) Fe and Cr, (d) Fe and (e) without any other minor constitute. The particle predominantly consists of C and O. Minor amounts of Si are

always present and may partly be an artifact of the substrate. Cu is an artifact from the TEM grid. Kα and Kβ as well as Lα and Lβ denote different X-ray peaks emitted from the same element.” EDX is a quantitative method. The height of individual peaks give a good estimate of the element abundance but is not linearly comparable because of different amounts of energy necessary to excite the individual elements; therefore every spectrum needs to be corrected in order to obtain quantitative amounts of elements. We introduced the following sentence to p.7 l.6 of the discussion paper: “Besides C, the refractory carbonaceous particles always contain O and Si (Figures 2, 4 and 5), and in most cases also S. The element Si may at least partly be an artifact of the substrate. The S X-ray peak in EDX-spectra originates either from sulfates internally mixed with the carbonaceous particles or from stray radiation. Please note that the heights of the individual peaks in figure 2 are not proportional to the element concentrations, but give a rough estimate of the element abundance.”

- Fig. 3: The given particle numbers are the total number of analyzed particles or only the refractory ones? Please specify this “n” in the figure caption.

We removed this figure from the manuscript for reasons given above.

- Fig. 6: The colors in the lower row of pictures are hard to see. I believe to use bright red or even white as occurrence indicator color in all pictures would improve the figure.

We agree. We decided to choose black/white.

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