

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

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We gratefully acknowledge the suggestions of the anonymous Referee I 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 #1

This manuscript describes electron microscopy of particles sampled from the polar stratosphere. It posits the existence of a new class of particles there, small refractory particles with high carbon content. If correct, these measurements are important for understanding aerosols in the polar stratosphere. For reasons given below, the data are quite implausible, but neither is there anything definitely wrong. I have comments in

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three areas: technique, plausibility, and minor comments. If this is published, it should be more in the tone of “we have some observations we don’t trust and definitely don’t understand, but they are the only observations we have”.

1) Technique.

a) The samples are from 2000, and the analyses appear recent. Does this mean the samples were stored in plastic boxes at room temperature for roughly 15 years before analysis? It might not be a problem, or there could possibly be artifacts from odd things like chemical interactions with vapors from the plastic box. Please comment in the manuscript.

The samples were collected in 2000, analysis started late in 2013. We found the samples after storage in a desiccator and 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.”

b) Are there any control samples? The manuscript mentions filter blanks, which are different than controls. Confidence in the results would be higher if samples from a

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known environment (for example, in the troposphere) gave the known results.

Unfortunately there are no control samples available. This is something we are aware of, and changed in recent campaigns, but can't change for past actions. The filter blanks the reviewer mentions proceeded the same actions as the real samples, e.g. equipping to the MACS, taking part in the sampling procedure without being exposed to ambient air, disassembly, storage, handling for measurements and measuring the samples themselves.

c) Can you define "refractory" more quantitatively? If a particle doesn't evaporate under the electron beam in vacuum, what does that mean in terms of carbonaceous material? Something with just a moderately high molecular weight, or does "refractory" mean it is practically a carbonate rock? Where would typical secondary organic material fall?

We do know many carbonaceous materials, e.g. soot, spores, fragments of plants, . . . which are stable under the high vacuum conditions in SEM and under the electron beam and which are thus identified to be refractory. But based on both the size and morphology of the particles, we can exclude all those particle species to be the same as the particles found in the current study. Furthermore, we do know that highly volatile material evaporates under both conditions in SEM mentioned. But unfortunately it is difficult to quantify the real nature of the carbonaceous particles. Regarding the definition of "refractory" we added a sentence to chapter 2.2: ". Similar to Ebert et al., 2016, we have classified all particles that are stable (no visible morphological change) under the high vacuum conditions and electron beam excitation in the SEM and TEM as refractory." Based on our long-lasting experience with tropospheric particles we know, that secondary organic materials (except soot) easily evaporates under the electron beam and does, thus, not show any "refractory" behavior. In addition, it would be questionable where the minor amounts of the elements Fe/Cr/Ni/Si found in the current study should come from in case of condensation (?) of secondary organic material.

2) Plausibility.

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a) I don't understand the lack of sulfur in the particles. In Figure 7, for most particles sulfur is below the detection limit of about 0.1%. The polar stratosphere vortex is a region of condensation of H₂SO₄ that had evaporated and photolyzed in the upper stratosphere (Mills, 2005 and references therein). At the concentrations modeled by Mills et al., it would take perhaps a week for enough H₂SO₄ to condense on a 100 nm particle to produce more sulfur than observed. This is a rough calculation, and the calculations by Mills span quite a range. Still, it underscores the difficulty of explaining why sulfur is below detection limit on most of the particles. Any particle that spent a significant amount of time in the polar stratosphere should have some sulfate, and sub-100 nm particles with high surface-to-volume ratios should have measurable amounts of condensing material.

We agree. As counting statistics might bear large errors based on impaction of several liquid H₂SO₄-droplets on the same spot, fast evaporation of small particles as well as fast evaporation in the vacuum chamber in the electron microscope leading to an underestimation of volatile particles, we decided to remove (the old) figure 3 from the manuscript. Furthermore, also very thin layers of volatile material on some of the refractory particles may have vaporized under the high vacuum conditions in the electron microscope. As each sample was at least equipped to the microscope for three times (first scan, measurement by SEM, measurement by TEM), this effect is likely to occur and may explain the low amount of S in (the new) figure 6. Anyhow, we are aware of the fact, that many more of the externally mixed carbonaceous particles should show some sulfur coating and thus discuss this issue in the text: "Most of the refractory carbonaceous particles are not included in or coated by sulfate. This is surprising, as the particles were sampled in air having low abundance of N₂O and therefore long residence times in the stratosphere (Table 1). Therefore, one would expect that all refractory particles occurring in the polar stratosphere are covered by sulfuric or nitric acid. The low abundance of refractory particles internally mixed with sulfates contradicts expectations based on the models by Mills et al. (2005) as well as the findings of Sheridan et al. (1994) and Murphy et al. (2013) which suggest that most or all strato-

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spheric refractory particles should be embedded in or coated with sulfuric acid. The results of our study can partly be explained by the evaporation of the sulfate component in the electron beam prior to its identification. The mixing state of the refractory carbonaceous particles may also be caused by splattering of volatile material of previously internally mixed refractory/volatile material. However, the reason for most of the refractory carbonaceous particles to be externally mixed remains open.”

b) I also don't understand the lack of any difference in composition between the inside and outside of the vortex (abstract and Figure 9). Curtius et al. (2005) found some big differences in refractory fraction between the inside and outside of the vortex. Yet in this manuscript there is no difference in composition. Nor is there any obvious correlation between the potential vorticity (PV) of samples with the volatile fraction (Table 1 and Figure 3). The samples listed with the highest volatile fraction (G and H) are inside the vortex, in apparent contradiction to Curtius et al.

The comparison of our data deduced from SEM-measurements are probably difficult to compare to COPAS-data from Curtius et al. (2005). The Aerosol preheater operated with COPAS forces volatile aerosol compounds to evaporate within 1 -2 seconds while exposed to temperatures of $\sim 250^{\circ}\text{C}$ – that this technique works to evaporate H_2SO_4 of stratospheric sizes to sizes below the COPAS detection limit was demonstrated to perform well (cf. Weigel et al. 2009). This kind of “flash”-evaporation by using thermo-denuders may force any solvent within a H_2SO_4 particle to get stuck together (including also insoluble incorporations) due to the surface tension of the evaporating H_2SO_4 . The identical instrument as used by Curtius et al 2005 was also deployed for the refining study Weigel et al. 2014. Thus a comparison of results seem to be most appropriate between these studies only.

The impactor sample technique and offline analysis, in contrast, may imply a very different process of separating volatile (mostly liquid) substances from incorporations of the stratospheric aerosol. The mostly liquid stratospheric particle literally smashes on the impactation plate such that liquid compounds with solvents as well as solid incorpora-

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tions are dispersed over a certain impact area on the substrate. Thus, the contributions of H_2SO_4 solvents may remain included in the H_2SO_4 matrix while all insoluble incorporation of the initial stratospheric aerosol particle are present as kind of debris field on the substrate surface to be analyzed.

In essence, the contribution (by number) of solvents to the “flash”-evaporized residual (COPAS technique) is not quantifiable and may vary from measurements in- and outside of the polar vortex. Such differences may be detectable when measured with 1Hz resolution (COPAS). Such differences (by number) of refractory aerosol, however, may not be resolved by aerosol samples in- and outside the polar vortex (due to e.g. sampling times over minutes) which was, furthermore, not the intention to investigate with this study, but instead, to investigate potential differences in the chemical composition and/or physical nature of particles sampled in- or outside the polar vortex.

As explained in 2a) we removed figure 3 from the manuscript.

c) Neither rocket exhaust nor extraterrestrial material are very consistent with the data. Kerosene rockets should produce soot, which was not observed. It is also doubtful that there are enough particulate emissions from non-solid-fuel rocket exhaust in the upper stratosphere to account for the observed particles. Note that the authors measured more carbonaceous material than meteor smoke. The authors could compare the estimated particulate emissions from rockets to the extraterrestrial flux to see if it is plausible that there is more carbonaceous material from rockets than meteoric smoke in the polar stratosphere. I tried a quick estimate and I don't think there is enough exhaust compared to meteor smoke, but I didn't spend much time tracking down references. Considering extraterrestrial material, there is too little Mg, Si, and Fe compared to carbon. For example, the carbon to silicon atomic ratio in micrometeorites collected in the stratosphere is about 1.3 to 2.4, (Shramm et al., 1989) but in these data it is over 30 (Figure 9). Even “carbonaceous” meteorites have more Mg, Si, and Fe than observed in these particles. In addition, the carbon in a meteoroid that got hot would oxidize to CO_2 and not produce particles. Submicron meteoroids don't get all that hot.

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So the particles would have to come from a cloud of submicron, organic particles in space around the Earth. I'm not a space scientist, but it seems that if such a cloud existed it would be known from effects on the near-Earth space environment.

Regarding rocket exhaust we have changed the last sentences to: "As the refractory carbonaceous particles observed by us are not soot, their origin from rocket exhaust is unlikely. However, as carbonaceous rocket exhaust particles were not investigated previously by electron microscopy this source cannot be excluded." Based on the interactive comment posted by Alexander D. James, we added a new paragraph to the "extraterrestrial material" section: "The chemical composition of extraterrestrial material may be strongly fractionated by frictional heating during atmospheric entry (e.g., Carrillo-Sánchez et al., 2016; Gómez- Martín et al., 2017). The processes taking place during atmospheric entry include ablation by sputtering and thermal evaporation as well as fragmentation. Meteorite ablation particles usually occur as iron, glass or silicate spheres (e.g., Blanchard et al., 1980; Murrell et al., 1980). Submicrometer refractory carbonaceous particles resulting from meteoric ablation and fragmentation have - to the best of our knowledge - not been described in previous literature. However, it is conceivable that such particles originate from carbonaceous material contained in meteorites or interplanetary dust particles. The observed non-chondritic ratios of the minor elements Fe, Cr, Ni are not a strong argument against such an origin, as the volatility of these elements depends on the minerals in which they are contained. Most of extraterrestrial Fe occurs as metal, silicate or oxide, most of Ni as metal (Papike, 1998). Cr may occur as oxide, sulphide or nitride as well as a minor component in metal and silicates (Bunch and Olsen, 1975). Depending on the relative abundance of the different mineral phases, substantial fractionation during evaporation can be expected (see also Floss et al., 1996). In summary, meteoric ablation and fragmentation particles are a possible source of the particles encountered in the present study."

3) Minor comments.

a) The units are incorrect on the extraterrestrial mass flux (line 25 page 11).

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The unit was corrected to 5-270 tons per day.

b) The discussion of sources only includes primary sources. What about secondary organics? Depending on the answer to my question about refractory organics, I would suggest that the authors consider secondary organic material more seriously, either formed in the troposphere or stratosphere.

We agree that secondary organic material, either formed in the troposphere or stratosphere, can serve as a source for carbonaceous particles in the stratosphere. As mentioned in 1c) the secondary material we know from our experience with tropospheric samples is highly volatile under high vacuum conditions and evaporates rapidly when measured by EDX. If the same processes and/or precursor gases make up secondary organic material in the stratosphere, then we expect the probability of the particles to originate from SOA to be low. As we cannot totally deny this possibility, we have changed p. 10 l. 19 based on Reviewer 2 to "Mixed carbon-sulfur particles were observed by Nguyen et al. (2008) (diameter $\leq 1 \mu\text{m}$) 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."

c) Can the authors estimate a mass mixing ratio for these particles, even to an order of magnitude?

Based on the impactor flow, we can roughly estimate a mass mixing ratio of the particles. Again, we have to emphasize that the errors of this estimate are large. The mass mixing ratio of the refractory carbonaceous particles varies between 0.65 (sample B) and 2.3 (mg air)⁻¹ (sample D) with a median for all samples of 1.1 (mg air)⁻¹. We included one additional paragraph in the introductory part of chapter 3: "Given the size of

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the refractory particles and the performance of the impactor, all similar particles in the sampled air were likely delivered to the impactor and collected there. Since the amount of air drawn through the impactor is known, the atmospheric abundance of these particles can be estimated from the number of particles in the impactor sample. That number was estimated from electron micrographs sampling the impactation spot and the size of the impactation spot. The ambient number mixing ratio of the refractory carbonaceous particles varies between 0.65 (mg air)⁻¹ and 2.3 (mg air)⁻¹, with a median for all samples of 1.1 (mg air)⁻¹ (Table 1). When compared with CPC measurements in Table 1, the carbonaceous particles comprised a few percent of the total number of particles in the air.” Furthermore we discuss the mass flux at the end of section 4.1: “In summary, the sole occurrence of refractory carbonaceous particles and sulfates in stratospheric samples was reported in previous literature but seems to be uncommon. The median number mixing ratio (1.1 mg air⁻¹) of carbonaceous particles is smaller by an order of magnitude than the abundance of non-volatile particles reported by, e.g., Weigel et al. (2014) for measurements in the winter stratospheric polar vortex in 2003, 2010 and 2011. The method described by Weigel et al. involves exposure of particles to a temperature >250 °C and determination (with a CPC) of the number of particles that did not evaporate to sizes below the detection limit of the CPC. They concluded that up to 80% of the particles present were non-volatile by this criterion. Following our definition only a few percent of the SOLVE particles are non-volatile in the electron microscope. This discrepancy may be caused by the different definitions of a non-volatile particle.”

d) Comparisons to other data could benefit from more attention to the size ranges and definition of “refractory.” For example, CN measurements consider a particle with 8 nm worth of nonvolatile material as refractory, these data would not. Both the Murphy et al. and Renard et al. data are only for larger particles than the ~100 nm particles described in this manuscript. The Zolensky et al. (1989) paper is about particles that are so much bigger it is just confusing to mention them.

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We agree that the particles detected by Murphy et al. regard basically size ranges ≥ 200 nm, up to several micrometers and those described by Renard et al. (2008) up to 350 nm. In more recent papers (Murphy et al., 2013) the authors were able to detect particles from 120 nm. Therefore the size ranges by the authors mentioned were added in the introduction, as well as in the discussion. Anyhow, an overlap of the size ranges of particles exist for sizes between ~120 – 800 nm and therefore we find the comparison of data by the mentioned authors meaningful. As the introduction is about general sources of particles in the stratosphere, we decided to leave the paragraph regarding rocket exhaust from Zolensky et al. (1989). In the paragraph regarding rocket exhaust as a potential source for stratospheric particles, the comparison to Zolensky et al. is used in the manner of showing, that rocket exhaust primarily emits characteristic Al₂O₃ spheres, which were not found in this study. There we do not compare them to carbonaceous particles but give a general statement on typical emissions by rockets. Therefore we also intended to leave the citation where it is.

e) The data could benefit from plotting the samples against a tracer or depth into the vortex instead of just “inside” and “outside”, or color-coding them on existing plots. I believe that N₂O was measured during SOLVE.

We agree. For clarity, we added the N₂O-values in Table 1.

Curtius et al., Observations of meteoric material and implications for aerosol nucleation in the winter Arctic lower stratosphere derived from in situ particle measurements, ACP, 2005.

Mills et al., Photolysis of sulfuric acid vapor by visible light as a source of the polar stratospheric CN layer, JGR, 2005.

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