

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

Answers to 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 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 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.

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 stratospheric 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 ~250°C – that this technique works to evaporate H₂SO₄ 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 H₂SO₄ particle to get stuck together (including also insoluble incorporations) due to the surface tension of the evaporating H₂SO₄. 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 impaction plate such that liquid compounds with solvents as well as solid incorporations are dispersed over a certain impact area on the substrate. Thus, the contributions of H₂SO₄ solvents may remain included in the H₂SO₄ 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 CO₂ and not produce particles. Submicron meteoroids don't get all that hot. 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-Martin 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).

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 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 impaction spot and the size of the impaction 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.

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.

Interactive comment on Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2017-278, 2017.

Answer to 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 were 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 were 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 were 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.

Table 2: Overview over particle parameters investigated.

Information	Number of particles investigated	Applied in Figure/Table	Method
Size, morphology, chemical composition	529	Figure 3	TEM
Mixing state, morphology	3316	---	
Nanostructure	23	Table 4, Figure 7	
Distribution of elements within the particles	4	Figure 5	STEM
Size, morphology, chemical composition	330	Figure 3, Figure 4, Figure 6, Figure 8	SEM
Sum of total particles	4202		

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 l. 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. 21: The ratios to C: It would help the reader's imagination if you would provide the ratios as a 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 assess 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 much 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. 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. 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. 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:

Table S2: Comparison of element ratios (median)

Element ratio	SEM	TEM
O/C	0.117	0.236
Si/C	0.065	0.161
S/C	0.004	0.013
Mg/C	-	$6.43 \cdot 10^{-4}$
Fe/C	0.012	0.114
Al/C	0.004	0.004

- p. 6 1. 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 impactation spot having a diameter of ~350 μm ."

- p. 6 1. 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 N_2O 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 N_2O .

- p. 7 1. 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 1. 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 inclusions 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, NO_y, were abundant. As we found the refractory carbonaceous particles in all samples independent of the occurrence of NO_y, they are not artifacts from the removal of material from the inlet system.”

- p. 7 1. 24: For how many particles was this element distribution image 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 Fig. 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 $\leq 1 \mu\text{m}$) 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."

- 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 burning, 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 1. 3: “sulfur” is an “element”, not a “component”. **Changed accordingly**

- p. 2 1. 13: which “groups” were 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 $\geq 0.35 \mu\text{m}$ (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. $dN/d\log D_p$. **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 $K\alpha$ and $K\beta$ 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. $K\alpha$ and $K\beta$ as well as $L\alpha$ and $L\beta$ denote different X-ray peaks emitted from the same element.**"

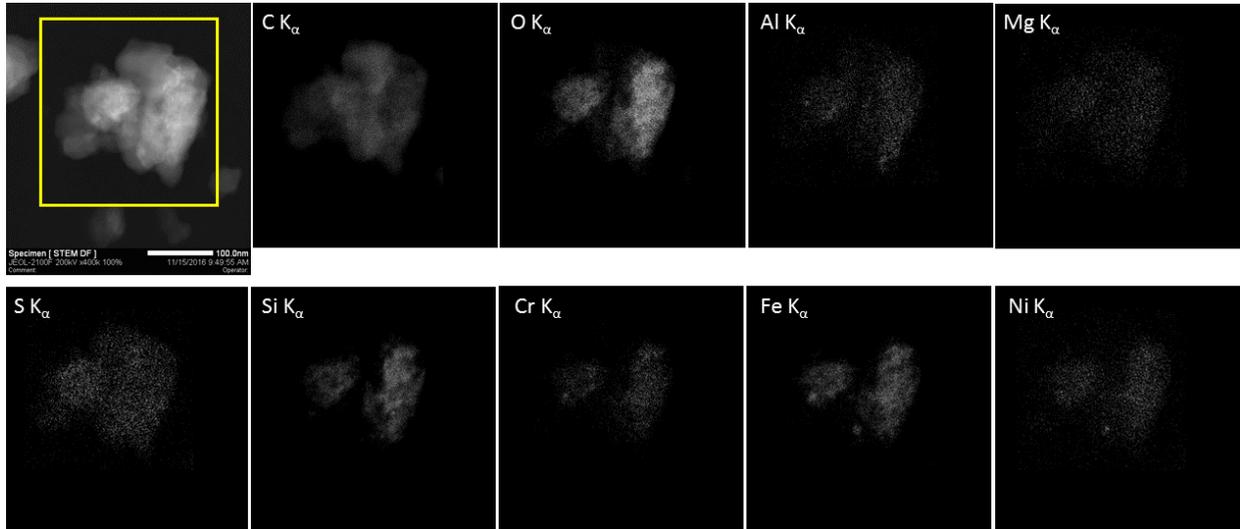
EDX is a quantitative method. The height of individual peaks give a good estimate of the element abundance but is not linearly comparable because of different amounts of energy necessary to excite the individual elements; therefore every spectrum needs to be corrected in order to obtain quantitative amounts of elements. We introduced the following sentence to p.7 I.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. The image now looks like the following:



List of relevant changes in the manuscript

- We have changed the manuscript title to „Sub-micrometer refractory carbonaceous particles in the polar stratosphere“
- Additional information is now provided in table 1: Sampling inside or outside of polar vortex, CPC Aerosol number mixing ratio, number of particles per milligram of air (mg air^{-1}), N_2O -values, age of air.
- Additional information on sample storage is now provided at the end of chapter 2.1. There we also provide literature information, that a change in particle morphology and nanostructure during the time of storage is not expected.
- Table 2 now provides information on how many particles were investigated with which method.
- S2 was added to the electronic supplement, showing a comparison of element ratios investigated by TEM and SEM
- We now estimated and added a median mass mixing ratio of the refractory carbonaceous particles of $1.1 (\text{mg air})^{-1}$.
- In chapter 3: „SEM Analysis of the chemical composition of the refractory carbonaceous particles“ we explain that the minor elements Fe, Cr and Ni only occur within the matrix of the refractory carbonaceous particles 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). Also, none of the samples was collected during the existence of ice particles which could potentially remove material from the impactors' inlet.
- We removed (the old) figure 3 from the manuscript.
- We now discuss the unexpected finding that most of the refractory carbonaceous particles are not included in or coated by sulfate even if the particles were sampled in air having low abundance of N_2O and therefore long residence times in the stratosphere (Table 1) at the beginning of chapter 4.1.
- We provide information of soot particle diameters that have been detected in the stratosphere in previous studies.
- We added the conclusion that we cannot totally exclude the possibility of our particles to be different to the ones found by Nguyen et al. (2009).
- We added the conclusion that 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 discrepancy is probably caused by the difference of the definition of non-volatile particles.
- We added an additional paragraph to chapter 4.2 “extraterrestrial particles”, discussing the possibility (based on the interactive comment of Alexander D. James) that recondensed organic matter and extraterrestrial particles, potentially originating from ablation and fragmentation may be a potential sources of the refractory carbonaceous particles.

Marked version of the script

Sub-micrometer refractory carbonaceous particles in the polar stratosphere

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Abstract. Eleven particle samples collected in the polar stratosphere during SOLVE (SAGE III Ozone loss and validation experiment) from January until March 2000 were characterized in detail by high-resolution transmission and scanning electron microscopy (TEM/SEM) combined with energy-dispersive X-ray microanalysis. A total number of 4202 particles (TEM=3872; SEM=330) was analyzed from these samples which were collected mostly inside the polar vortex in the altitude range between 17.3 and 19.9 km. Particles that were volatile in the microscope beams contained ammonium sulfates and hydrogen sulfates and dominated the samples. Some particles with diameters ranging from 20 to 830 nm were refractory in the electron beams. Carbonaceous particles containing additional elements to C and O comprised from 72% to 100% of the refractory particles. The rest were internal mixtures of these materials with sulfates. The median number mixing ratio of the refractory particles, expressed in units of particles per milligram of air, was $1.1 \text{ (mg air)}^{-1}$ and varied between 0.65 and $2.3 \text{ (mg air)}^{-1}$.

Most of the refractory carbonaceous particles are completely amorphous, a few of the particles are partly ordered with a graphene sheet separation distance of $0.37 \pm 0.06 \text{ nm}$ (mean value \pm standard deviation). Carbon and oxygen are the only detected major elements with an atomic O/C ratio of 0.11 ± 0.07 . Minor elements observed include Si, S, Fe, Cr and Ni with the following atomic ratios relative to C: Si/C: 0.010 ± 0.011 ; S/C: 0.0007 ± 0.0015 ; Fe/C: 0.0052 ± 0.0074 ; Cr/C: 0.0012 ± 0.0017 ; Ni/C: 0.0006 ± 0.0011 (all mean values \pm standard deviation).

High resolution element distribution images reveal that the minor elements are distributed within the carbonaceous matrix, i.e., heterogeneous inclusions are not observed. No difference in size, nanostructure and elemental composition was found between particles collected inside and outside the polar vortex.

Based on chemistry and nanostructure, aircraft exhaust, volcanic emissions and biomass burning can certainly be excluded as source. The same is true for the less probable, but globally important sources: wood burning, coal burning, diesel engines and ship emissions.

Recondensed organic matter and extraterrestrial particles, potentially originating from ablation and fragmentation remain as possible sources of the refractory carbonaceous particles studied. However, additional work is required in order to identify the sources unequivocally.

1 Introduction

The chemistry of stratospheric aerosols has been studied for more than half a century (Junge et al., 1961; Junge 1963), and it was discovered that sulfur is the main element in the particles. Junge and Manson (1961) supposed the particles to consist of ammonium sulfate, and Bigg et al. (1970) suggested sulfuric acid with varying amounts of ammonia. Rosen et al. (1971) strengthened the evidence for the material to be sulfuric acid as most of the material evaporated at the temperature expected for this substance. According to Bigg (1975), the majority of the particles is composed of sulfuric acid with varying amounts of ammonium sulfate. A comprehensive summary of stratospheric aerosol and sulfur chemistry is given by Kremser et al. (2016).

In addition to the dominating sulfur-rich particles (sulfuric acid, sulfates), refractory particles were reported frequently. Dense, mineral-rich particles presumably originating from the eruption of the Mt. Agung volcano were observed by Mossop (1963, 1965) using scanning electron microscopy. However, due to the lack of instrumentation, the chemistry of the particles could not be investigated. Refractory particles with diameters $>1 \mu\text{m}$ were studied in more detail by Zolensky and Mackinnon (1985), and several particle groups were distinguished: chondrite, silicate, aluminum (Al), aluminum with variable amounts of other elements, iron (Fe) with or without sulfate (S), calcium (Ca)-Al silicates and “other” particles. The silicate particles were dominant and interpreted to be volcanic, probably from the Mt. St. Helens eruption in 1980. In contrast to prior findings, a large number of refractory stratospheric particles was recognized by Zolensky et al. (1989). The particles they analyzed had diameters of $>> 1 \mu\text{m}$. The authors assumed that this increase was caused by solid rocket exhaust or the re-entry of debris associated to human space flight activity (inoperative satellites, burnt out rocket stages, tools, etc.). According to Sheridan et al. (1994) approximately 97% of all analyzed stratospheric particles were sulfuric acid. Also non-sulfate materials, soot, other C-rich substances and crustal material were detected. 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 $\geq 0.35 \mu\text{m}$ (Renard et al., 2008). Della Corte et al., 2013 found calcium-oxygen (CaO) -rich particles probably originating from a bolide that penetrated the Earth’s atmosphere. Single particle mass spectrometry (SPMS) brought new insights into the chemistry of stratospheric particles (e.g., Murphy et al., 1998, 2007, 2013). The method is capable to measure particles in the size range of 120 nm – 3 μm (with a very low detection efficiency for particles $< 220 \text{ nm}$; Murphy et al., 2007). According to these authors, stratospheric particles are dominated by pure sulfuric acid, sulfuric acid internally mixed with material from ablated meteoroids, and mixtures of organic-sulfate particles. A recent SEM study by Ebert et al. (2016) focused on refractory particles in the late winter stratospheric polar vortex. The main particle groups encountered included Fe-rich, Si-rich, Ca-rich, metal mixtures and Carbon (C)/Si-rich particles.

Refractory particles in the UT/LS (Upper Troposphere / Lower Stratosphere) can act as condensation nuclei for cirrus clouds (Kojima et al., 2004; 2005; Cziczo et al., 2013) and as surfaces for heterogeneous chemical reactions in the polar stratosphere which play a significant role in polar ozone depletion (e.g., Peter, 1997; Solomon, 1999; Peter and Grooß, 2012). In addition, the particles can serve as surfaces for the heterogeneous condensation of saturated gases in the polar stratosphere (Saunders et al. 2010, 2012; Voigt et al. 2005). Due to the acidic environment, the

particles can (partially) dissolve in the acidic solution droplets (binary $\text{HNO}_3\text{-H}_2\text{O}$ or ternary $\text{HNO}_3\text{-H}_2\text{SO}_4\text{-H}_2\text{O}$) and, thus, change their freezing properties. Therefore, the dissolved particles in a ternary $\text{HNO}_3\text{-H}_2\text{SO}_4\text{-H}_2\text{O}$ solution could have an important impact on the formation of polar stratospheric clouds (PSCs). As gaseous compounds will condense on refractory particles, they will grow, both in size and mass, which leads to a change in their sedimentation velocity (Fromm et al. 2000; Jost et al., 2004). Therefore, the gaseous compounds can **both** be redistributed in the stratospheric region **and** sediment out more quickly.

There are multiple sources which contribute to the stratospheric refractory particle load. Interplanetary dust particles are considered to be the major component of refractory material (Murphy et al., 1998; 2007; Plane, 2012). Another important source of stratospheric refractory particles are volcanic eruptions which may either eject material directly into the stratosphere (Vernier et al., 2011) or lead to particle transport through the tropical transition layer (TTL) (Mattis et al., 2010). Further potential sources of stratospheric refractory particles are high-flying aircraft (Fahey et al, 1995; Pueschel et al., 1997, Petzold et al., 1999), rockets (Newman et al., 2001), ablated material from meteorites (Hunten et al. 1980; Turco et al., 1981; Murphy et al., 1998; Cziczo et al., 2001) and all kinds of terrestrial material being lifted and entrained into the stratosphere by the Brewer-Dobson-Circulation (Holton et al., 1995, Austin and Li, 2006). **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.**

In summary, a variety of different refractory particle types is observed in the stratosphere. Due to the still limited number of sampling and measurement campaigns, the occurrence as well as the sources of refractory particles is not known precisely. The present paper first aims at improving the database on the observed particle groups. Second, it is attempted to infer potential sources by a detailed characterization using high-resolution transmission electron microscopy (TEM), scanning electron microscopy (SEM) and energy-dispersive X-ray microanalysis (EDX).

2 Experimental

2.1 Sampling

Stratospheric particles were sampled on board of the NASA ER-2 aircraft during the SAGE III Ozone loss and validation experiment (SOLVE), which was conducted in January-March 2000 in Kiruna (Sweden). **The Multi-Sample Aerosol Collection System (MACS) (Kojima et al., 2004), a thin-plate low-pressure impactor, was used for sampling. The particles were deposited on TEM copper (Cu) grids covered with a formvar film. MACS is designed to collect up to 23 samples per flight. The first sample is not exposed to flow and serves as a blank sample. The MACS was designed to sample and transmit all particles in the diameter range from 20 to 1000 nm to the impactor. Particles larger than approximately 20 nm are collected on the impactor in the pressure range shown in Table 1. In situ measurements of aerosol abundance were obtained with a Condensation Particle Counter (Wilson et al., 1983) simultaneously with the samples. Sampling date, flight characteristics, potential vorticity (PV), pressure altitude, pressure, potential temperature and ambient aerosol number mixing ratio (particles per milligram of air) for the analyzed samples are shown in Table 1. In situ detection of nitrogen oxides on particles (Fahey et al., 2001) was used to determine if samples were collected when the aircraft was in polar stratospheric clouds (PSCs) containing**

nitrogen. Measurements of N₂O provide insight into the residence time of the air parcel in the stratosphere, called age of air (Wilson et al., 2008). These values are also shown in Table 1.

The meteorological conditions of the early winter (November – January) northern hemispheric polar vortex of 1999/2000 are described in detail by Manney and Sabutis, 2000. The early winter (November – January) northern hemispheric polar vortex of 1999/2000 had much lower averaged temperatures compared to any previously observed Arctic winter. The vortex was weaker than the early winter polar vortices of the previous years. It was discontinuous in the middle of December, with a large extent in the upper and small extent in the lower stratosphere. 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). Jost et al. (2002) describe anomalous single mixing events occurring during that time at the potential temperature (Θ) range of 350-500 K. These events are probably the result of mixing between deep vortex and extra vortex air.

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. In total, 122 samples from 15 sampling days were collected.

2.2 Electron microscopy

A total of 4202 particles (3872 TEM; 330 SEM) from 11 samples were investigated by transmission and scanning electron microscopy. The samples were selected according to meteorological conditions and suitability for electron microscopy (i.e., substrate area covered by particles). Table 2 gives an overview on how many particles were investigated with which method.

The objective of this study is the detailed characterization of refractory stratospheric particles. 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.

The size, morphology, mixing state, nanostructure and chemical composition of 60 refractory particles per sample were studied by TEM using a Philips CM20 instrument (FEI, Eindhoven, The Netherlands) operated at 200 kV electron accelerating voltage. The chemical composition of the particles (all elements with an atomic number $Z \geq 5$) was determined by EDX using a Silicon-drift X-ray detector (Oxford Instruments, Oxfordshire, United Kingdom) and a measurement time of 20 seconds. Particle size and graphene sheet separation distance were analyzed by the ImageJ software (1.48v; Rasband, W. S. National Institutes of Health, USA, 1997-2016). Element distribution images were acquired with a JEOL JEM 2100F (JEOL, Tokyo, Japan) operated in Scanning Transmission Electron Microscopy (STEM) mode at an electron acceleration voltage of 200 kV. The instrument is equipped with the same type of EDX-detector as the Philips CM20 instrument.

In order to detect elements present at low abundance, additional 30 refractory particles per sample were analyzed by SEM using a Quanta 200 FEG instrument (FEI, Eindhoven, The Netherlands) equipped with an EDX detector (EDAX, Tilburg, The Netherlands) operated at 15 kV electron accelerating voltage. X-ray spectra were accumulated over fifteen minutes per particle to obtain a low detection limit. These long exposures were not feasible in the TEM due to its higher beam energy and resulting particle evaporation. Element concentrations were obtained from the X-ray count rates by applying a “standard-less” ZAF correction. Detection limits of element/carbon ratios (at% / at%) for the long-time measurements are as follows: O/C = 0.0034; Si/C = 0.0010; S/C = 0.0008; Cr/C = 0.0008; Fe/C = 0.0009 and Ni/C = 0.0011.

The particles were studied by TEM and SEM without coating.

Potential contamination of the samples was checked by investigating blanks (samples transported in the MACS but not exposed to stratospheric air flowing through the impactor orifice) for each sampling day. A few titanium (Ti) and zinc (Zn) oxide particles, as well as few pure C particles were encountered on the blank samples. They look similar to some carbonaceous particles being described as contaminants on TEM grids (Harris et al., 2001). However, these particles are different in both size and morphology compared to the carbonaceous particles observed in the impaction spot of the samples.

In order to verify that the small amounts of Fe, chromium (Cr) and nickel (Ni) detected during long-term SEM measurements are not artifacts from the substrate, five points on each substrate far away from particles were analyzed. These three elements were not detected in the measurements of the clean substrates.

Another artefact can result from scattered radiation within the SEM. This could lead to the detection of chemical elements in the vacuum chamber’s housing material. To test this possibility, one sample was measured at larger sample chamber pressures (5×10^{-3} , 200 and 500 Pa) which result in increased scattering of beam electrons in the sample chamber. According to Stokes (2008), scattering varies between 40 – 80 % at 200 Pa and 70 – 98 % at 500 Pa. Fe, Cr, and Ni did not show increased concentrations at higher pressure, but rather their count rates decreased. The small Fe, Cr and Ni concentrations detected in individual particles were not the result of stray radiation.

The elemental composition of the particles was determined by EDX in TEM (n = 529) as well as SEM (n = 330). Due to the small size of the particles, TEM is the preferred method of analysis. As mentioned above, particles were additionally analyzed by SEM. Both measurements led to small but systematic differences in the ratios of O, Si, S, Mg (magnesium), Fe and Al to C. For example, the median O/C value is 0.236 for TEM and 0.117 for SEM (Figure S1 and S2 of the electronic supplement). For all elements TEM-EDX yielded somewhat higher elemental ratios relative to carbon than SEM-EDX. These differences most likely result from differences in the detectors, such as thickness of detector windows, and the different acceleration voltages (15 kV in SEM versus 200 kV in TEM). However, as the differences are small (Figure S2 of the electronic supplement), our conclusions are independent of the method used. SEM-EDX data are reported here since the counting time on each particle was much longer in SEM (15 minutes) than in TEM (20 seconds) leading to higher precision as well as lower detection limits. The much lower detection limits of SEM-EDX are important for source identification as minor elements may serve as fingerprint for several anthropogenic and natural sources. Thus, the SEM-EDX data are preferred despite the lower number of particles investigated with this technique. In addition, the chemical composition of particles could not be analyzed by

TEM-EDX on two samples (labeled as G and K) due to the inappropriate position of the impaction spot on the substrate (too close to the Cu grid leading to a very high count rate for Cu).

In order to assess the mixing state of the refractory particles, additional image analysis was performed in TEM. For this purpose image series before and after TEM analysis were prepared.

All particles which showed no signs of destruction or morphological change were defined as refractory. Particles which changed under the electron beam were deemed volatile, allowing quantification of the fraction of aerosol which is volatile. In total 3316 particles were analyzed by this method.

To ensure unbiased results, the individual images as well as particles for EDX analysis were randomly taken in inner and outer areas of the impaction spot.

2.3 Statistical analysis

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).

3 Results

All collected particles are located within a characteristic impaction spot having a diameter of ~350 μm . As TEM bright field images show (Figure 1), volatile particles (initially deposited as droplets) cover a relatively larger area compared to refractory particles. They show high abundances of sulfur and oxygen. Sometimes, a minor nitrogen peak is also observed in the X-ray spectra. These particles are highly unstable under electron bombardment. They most likely consist of ammonium sulfate/hydrogen sulfate and formed from sulfuric/nitric acid. As the presence of sulfates in stratospheric samples is well known (e.g., Sheridan et al., 1994; Arnold et al., 1998; Murphy et al., 2007; Kremser et al., 2016), these particles are not investigated further. In addition to the sulfates, carbonaceous particles stable under electron bombardment are frequently observed either as individual particles or embedded in the sulfates (Figures 1 and 2).

As the refractory carbonaceous particles in Figure 2a have no distinct shape and surface morphology, only one TEM image is shown.

Given the size of 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 impaction spot and the size of the impaction spot. The ambient number mixing ratio of the refractory carbonaceous particles varies between $0.65 \text{ (mg air)}^{-1}$ and $2.3 \text{ (mg air)}^{-1}$, with a median for all samples of $1.1 \text{ (mg air)}^{-1}$ (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.

TEM Analysis of the size distribution of the particles

The size distribution of the refractory carbonaceous particles is indicated in Figure 3. Approximately 98 % of the particles have an equivalent projected area diameter (D_{pa}) below 500 nm (range 20 – 830 nm). The size of the particles slightly increases with time during the campaign, sample J shows the largest median particle sizes.

SEM Analysis of the chemical composition of the refractory carbonaceous particles

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, NO_y , were abundant. As we found the refractory carbonaceous particles in all samples independent of the occurrence of NO_y , they are not artifacts from the removal of material from the inlet system. As the TEM substrates are made of a formvar foil predominantly consisting of C, O, and traces of Si, these three elements may – at least partly – be an artifact of the substrate. However, there are three points of evidence which clearly show that the refractory carbonaceous particles observed are not an artifact of the substrate:

- 1) Much higher carbon X-ray count rates were obtained when measuring particles compared to the pure substrate.
- 2) Graphene sheets within the particles were observed by high resolution TEM. In contrast, the substrate is always completely amorphous.
- 3) The refractory carbonaceous particles only occur within the impaction spot.

The refractory carbonaceous particles have a different morphology than the few carbonaceous particles found on blank samples. In addition, the carbonaceous particles encountered on blank samples are often much larger with a size of several μm . Please note that a different foil with much higher O and Si contents was used for sample K. Thus this sample was excluded from figures 4, 6 and 8. The TEM grids consist of Cu leading to strong Cu X-ray peaks in the spectra (Figure 2). Consequently, Cu is excluded from the further analysis and discussion. Mg is only present in a

few particles. S is the major component of the volatile material surrounding the carbonaceous particles. Fe is found as a minor element in the majority (~ 95 %), Cr in about 87 % and Ni in about 49 % of refractory particles.

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. The elements O, Si, Cr and Fe only occur in some regions of the particles. The element Al is only detected in few particles. Due to the low number of X-ray counts, the distribution of Mg and Ni is difficult to assess. S seems to occur in the whole particle and is assumed to come from stray radiation of the surrounding sulfates. The heterogeneous element distribution was also observed in multiple point measurements (up to 20 points on one particle).

Based on elemental composition, the refractory carbonaceous particles (number $n = 330$) were classified into four groups (Table 3). Only few particles consist of C, O, and Si only. Many particles contain additional Cr, Fe and Ni ($n = 131$) or Cr and Fe ($n = 125$). Particles only containing additional Fe are rare ($n = 22$). Please note that the element S was not used for particle classification, because this element is found in most spectra, either due to scattering from surrounding volatile particles or because the refractory carbonaceous particles are embedded in sulfates.

Element ratios relative to C (at% / at%) are shown in Figure 6 for all samples. The median O/C ratio varies between 0.052 and 0.129. The median Si/C ratios vary between 0.003 and 0.012, but may be influenced by the substrate. For all other elements, the respective median ratios are generally very low (< 0.005). Sample K is not shown due to the different substrate used (with lower C and higher Si content). The differences between the various samples are for all element ratios statistically significant on the 5 % level. Most obvious, sample G has lower element/C ratios than the other samples.

TEM analysis of the particle nanostructure

The nanostructure was investigated by high resolution TEM. All particles are either completely amorphous (Figure 7 a, b) or show only very small regions (less than ten graphene sheets) with ordering (Figure 7 c, d). In the latter case, the graphene sheet separation distance was determined (Table 4). As these measurements are very time-consuming, only 23 particles from 5 samples were investigated. The graphene sheet separation distance varies between 0.19 and 0.60 nm, the mean values of different grains between 0.25 and 0.47 nm. This range is slightly larger than typically observed for soot (Vander Wal et al., 2010; Li et al., 2011; Liati et al., 2014; Weinbruch et al., 2016).

All samples, with the exception of one (sample D), were collected inside the polar vortex. Element ratios of the samples inside and outside the vortex are compared in Figure 8. There are no statistically significant differences on the 5% level in element ratios and particle size (Figure 3) between these two cases.

4. Discussion

4.1 Occurrence of refractory carbonaceous particles in the stratosphere

We find that all of the refractory particles are carbonaceous and typically contain minor amounts of Fe, Cr and Ni distributed within the particles. 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 stratospheric 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.

Refractory carbonaceous particles in the polar stratosphere were identified in several earlier studies (discussed below). Depending on the applied technique different terms were used for such particles. In the present contribution the following nomenclature is used: All particles consisting predominantly of the element carbon are termed carbonaceous, i.e., only the chemical composition is used for classification. The term soot is used for agglomerates of primary particles (20 – 50 nm size) predominantly consisting of carbon which show a specific, onion-shell like nanostructure (Buseck et al., 2012). Black carbon (BC) is used for particles strongly absorbing light in a wide spectrum of the visible wavelength (Petzold et al., 2013) with at least 5 m²g⁻¹ at a wavelength of 550 nm (Bond et al., 2013).

Soot in the stratosphere was previously identified by scanning and transmission electron microscopy in accordance with the nomenclature outlined above (Pueschel et al., 1992 (diameter = 0.2 – 0.3 μm), 1997 (diameter ≤ 1 μm); Sheridan et al., 1994 (diameter ~ 0.3 μm); Blake and Kato, 1995 (diameter ≤ 0.5 μm); Strawa et al., 1999 (diameter = 0.3 – 0.4 μm); Ebert et al., 2016 (diameter ≤ 0.5 μm)). Carbonaceous particles (diameter ~ 0.1 μm) which might be soot although they were not unequivocally identified as such, due to the lack of high resolution images, were found by Chuan and Woods (1984). Testa et al. (1990) found seven poorly graphitized carbon particles in their samples and regarded them as artifacts of carbon films from the TEM grids. As they did not provide images of these particles, they cannot be compared to our findings. However, we can exclude that our particles are substrate contaminants, since such particles did not occur on the blank samples. In addition, the refractory carbonaceous particles were only observed within the impaction spot and not on the clean substrate.

Carbonaceous particles partly containing heterogeneous metallic inclusions were found by Chen et al. (1998) (diameter = 0.1 – 2 μm). Some of these particles were called soot without providing a more precise description. Thus, it is not clear if they are similar to particles we identified as soot. According to these authors, the “soot particles” most likely stem from aircraft exhaust, as the samples were – at least partly – collected in the exhaust of an aircraft in the lower stratosphere.

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.

Stratospheric carbonaceous particles were also often detected by means of mass spectrometry (MS). For example, Murphy et al. (1998, 2013) identified carbonaceous particles, with a lower abundance in the stratosphere compared to the upper troposphere (Murphy et al., 2013; diameter = 0.3 – 0.8 μm ; tropics and mid-latitudes). The same group (Murphy et al., 2007) reported the presence of a small fraction of carbonaceous particles (diameter \leq 300 nm) within the stratosphere. As some of these particles contained potassium, they were assumed to originate from biomass burning. Particles from rocket and space shuttle exhaust (collected in the stratosphere) were investigated by Cziczo et al. (2002) with the same instrument. In solid fuel rocket exhaust (Athena rocket and space shuttle boosters) the most frequent observed signals stem from different aluminum oxide species (often with minor amounts of Fe). About 17% of the particles (Athena rocket) were classified as carbonaceous as compared to 1% from space shuttle exhaust. In principle, the carbonaceous particles found by MS could be similar to the carbonaceous particles of the present study. Since MS does not yield images of the particle morphology or information on the nanostructure, no definite conclusion can be drawn.

Stratospheric carbonaceous particles were also identified by optical measurements. For example, a single particle soot photometer (SP2) was applied by Baumgardner et al. (2004) (diameter = 0.15 – 1 μm) on board of an aircraft in order to identify ozone loss processes in the polar vortex. In total, 60% of the light absorbing particles incandesce at temperatures above 3500 K and are, thus, interpreted as BC. According to Baumgardner et al. (2004) these particles originate from tropospheric sources rather than aircraft emissions. The same technique was applied by Schwarz et al. (2006) (diameter = 0.15 – 0.7 μm) to identify BC in midlatitudes from the boundary layer to the lower stratosphere. Only \leq 1% of the particles was classified as BC and no potential source was specified.

Local enhancements of carbonaceous material at altitudes around 25 km were also deduced from simultaneous measurements of a spectrometer on board a satellite as well as from radiance and particle counter data (Renard et al., 2008) (diameter = 0.35 – 2 μm) obtained on a stratospheric balloon. This material was thought to be injected into the stratosphere by the pyro-convective effect (i.e., fire-started or fire added convection). Some of the particles with submicron size were supposed to originate from vaporized interplanetary material (Renard et al., 2008). Due to the lack of information on morphology, chemistry and microstructure of the particles, a direct comparison of the carbonaceous material deduced from optical measurements with the particles encountered in the present study is not possible.

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).

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 $>250 \text{ }^{\circ}\text{C}$ 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.

4.2 Potential Sources

The most likely sources of refractory carbonaceous particles found in the current study include aircraft emissions, extraterrestrial sources, rocket exhaust and explosive volcanic eruptions as these sources emit material directly into the stratosphere. In addition, biomass burning can be considered as a possible source, as it was shown by several authors that large fires have sufficient energy to inject particles into the lower stratosphere (Fromm et al., 2000, 2006, Siebert et al., 2000; Fromm and Servranckx, 2003; Jost et al., 2004; Siddaway et al., 2011). Domestic wood burning, coal combustion, diesel engines and ship exhaust are not expected to significantly contribute to the stratospheric particle load. However, as these sources emit large amounts of carbonaceous material on a global scale (Bond et al., 2004, Gaffney and Marley, 2005, Corbett and Koehler, 2003; Lauer et al., 2007), they will be discussed shortly. For example Thornberry et al., 2010 show that tropical tropospheric particles contain high amounts of thermostable carbonaceous material, and it is possible that these particles become mixed within stratospheric air. Although the vertical exchange may be less effective than the direct injection processes, however, it is conceivable that fractions of carbonaceous aerosol material released in the troposphere is vertically transported into the stratosphere by processes such as tropical convection (and lifted further via the Brewer-Dobson circulation), cyclogenesis, warm conveyor belts, tropopause folds and/or isentropic transport.

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.

Aircraft exhaust

High flying aircraft can contribute significantly to the stratospheric aerosol burden. Soot is described as the main particulate exhaust component (Twohy and Gandrud, 1998; Popovitcheva et al., 2000; Smekens et al., 2005; Vander Wal et al., 2010; Liati et al., 2014). The observed soot consisted of primary particles 10 - 50 nm in diameter which formed aggregates with diameters of up to approximately 450 nm (Twohy and Gandrud, 1998; Popovitcheva et al., 2000; Smekens et al., 2005; Liati et al., 2014). The nanostructure of the primary particles varied from an onion-shell structure with partial ordering (Popovitcheva et al., 2000; Vander Wal et al., 2010) to completely amorphous (Twohy and Gandrud, 1998). The mean graphene sheet separation distance of the partly ordered primary particles varied between 0.36 and 0.41 nm (Vander Wal et al., 2010; Liati et al., 2014). An atomic O/C ratio of 0.32 was reported by Vander Wal et al. (2010). The elements S, Na (sodium), N (nitrogen), Zn (zinc), Ba (barium), Cl (chlorine), K (potassium), Fe and Si were detected in minor concentrations (Vander Wal et al., 2010; Mazaheri et al., 2013). In addition to soot agglomerates, single carbon spheres were found by Mazaheri et al. (2013) in aircraft exhaust. The particles have diameters between 5-100 nm with a median of 35.4 nm. Besides C, minor O, S, Cl, K, Fe and Si were detected by TEM-EDX and Proton Induced X-ray Emission (PIXE) analysis. Aircraft exhaust is excluded as source of the carbonaceous particles encountered in the present study, as we did not observe soot agglomerates. In addition, the chemistry and morphology (basically rounded shapes) of the single carbon particles described by Mazaheri et al. (2013) are different from our particles.

Extraterrestrial particles

With an input of 5-270 tons per day (Plane, 2012), extraterrestrial material is expected to be the major source of refractory stratospheric particles (Murphy et al., 1998; 2007). Carbonaceous material is observed in chondrites (dominant meteorite fraction) as well as in interplanetary dust particles (IDPs).

In carbonaceous chondrites, a variety of different carbonaceous constituents is described in previous literature. For example, nanometer-sized carbon-rich flakes, spheres and tubes as well as hollow carbon-rich nanospheres were found (Garvie and Buseck, 2004; Garvie, 2006; Garvie et al., 2008). Most carbonaceous nanospheres are amorphous. Besides C, the only other elements detected are S, N and O. Carbonaceous material in carbonaceous chondrites was also investigated by Aoki and Akai (2008). Different morphologies like “ribbon-film-like carbonaceous material”, “spherical carbonaceous globules”, “concentric-sphere type carbon material”, and “featureless carbon material” were observed. They also describe the occurrence of minor amounts of Cl in many of these particles, an element never observed in our study. Neither morphology nor shape or chemical composition of the particles described above matches the refractory carbonaceous particles encountered in the present study. Carbon nanoparticles with diameters between 2-10 nm were observed in carbonaceous material isolated from the Allende carbonaceous chondrite (Harris et al., 2000). The particles had either a single outer wall or were surrounded by multiple walls. However, as the particles were mobile under the electron beam, no photographs are shown. A comparison to our particles is thus impossible. Since the authors did not find any other elements except C, most of our particles differ in chemical composition as they contain Fe, Cr, and/or Ni as minor elements.

Carbonaceous material was also found in IDPs (Matrajt et al., 2012). Some of the material observed is similar in size, morphology and nanostructure to our particles. However, in Matrajt et al. (2012) minor elements were not investigated and this parameter cannot be compared.

In summary, the carbonaceous components observed in chondrites differ in chemical composition from most of our particles. Carbonaceous material contained in IDPs cannot be excluded as source of the refractory particles encountered in the present study, as the minor element concentration of the former is not known. However, if we expect extraterrestrial material to be the major source of our particles, we would also expect to find Mg-rich silicates in our samples, which was not the case. Furthermore, the occurrence of Fe, Cr and Ni as minor elements in our refractory carbonaceous particles is regarded as hint for an anthropogenic origin. This interpretation is supported by the fact that the observed average atomic ratios of these three elements (Cr/Fe = 0.249, Ni/Fe = 0.167, Cr/Ni = 1.145) are significantly higher than the cosmic element ratios (Cr/Fe = 0.015, Ni/Fe = 0.056, Cr/Ni = 0.278; Palme and Jones, 2005).

The chemical composition of extraterrestrial material may be strongly fractionated by frictional heating during atmospheric entry (e.g., Carrillo-Sánchez et al., 2016; Gómez-Martin 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.

Rocket Exhaust

Rocket exhaust is also a possible source of stratospheric particles. However, literature on particles emitted by rockets is sparse (e.g. Zolensky et al., 1989), and there are – to the best of our knowledge – no studies available on carbonaceous particles by electron microscopy. According to Ross and Sheaffer (2014), five different propellant types which use a combination of different oxidizers and fuels are in use: O₂/kerosene, O₂/H₂, NH₄ClO₄/Al, N₂H₄/N₂O₄ and N₂O/solid hydrocarbons. Solid rocket motors (SRM) emit characteristic Al₂O₃ spheres (Strand et al., 1981; Zolensky et al., 1989; Cofer III et al., 1991) and can, thus, be excluded as source of the carbonaceous particles encountered in the present study. Hydrocarbon-fired rockets are powered by kerosene or synton and can be expected to emit soot. For example, soot particles most likely emitted by a Russian Soyuz booster rocket were found in an aerosol cloud at 20 km (Newman et al., 2001). The soot particles contribute approximately 1/4 to the total particle number, the rest were volatile sulfate particles. The occurrence of carbonaceous material from rocket exhaust was

also reported by Cziczo et al. (2002). In the exhaust of an Athena II rocket, the carbonaceous fraction of material was found to be 17% by number (Cziczo et al., 2002). 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.

Volcanic emissions

Volcanic eruptions are generally not considered to emit carbonaceous material. However, carbonaceous material was found in samples from the Kasatochi (Alaska, 2008), Sarychev (Russia, 2009) as well as Eyafjallajökull (Island, 2010) eruptions (Martinsson et al., 2009; Schmale et al.; 2010; Andersson et al., 2013). The carbonaceous material most probably originates from air entrained into the volcanic cloud. The carbonaceous mass fraction in plumes from two volcanoes in Ecuador and Columbia was found to vary between 19-38% (measured by MS; Carn et al., 2011). Sulfur-carbonaceous mixed particles occurred predominantly in the size range below 0.9 μm . In 1999, the year before the campaign, there were four volcanic eruptions with a $\text{VEI} \geq 4$ (Volcanic Explosivity Index): Soufrière Hills (West Indies) in January, Shiveluch (Russia) in August as well as Guagua Pichincha (Ecuador) and Tungurahua (Ecuador) in October (NOAA, 2017). Still, volcanism seems an unlikely source for our samples, as volcanic eruptions will emit large amounts of silicate particles, which we did not observe.

Biomass burning

A further source of carbonaceous particles in the stratosphere is biomass burning (BB). Particles originating from BB can be lifted to the stratosphere by either the tropical upper tropospheric upwelling or the pyroconvective effect (Fromm et al., 2000; Jost et al., 2004). Three different types of carbonaceous BB particles were described in previous literature (e.g., Pósfai et al., 2003; 2004; Kis et al., 2006; Li and Shao, 2009): organic particles with inorganic inclusions, tar ball particles and soot. Organic particles (no specific morphology) contain C and minor O, and are stable under the electron beam. They do not show the typical microstructure of soot (see below). The inorganic inclusions mostly consist of KCl and K_2SO_4 . Tar balls have a typical spherical shape and mainly consist of C and O with minor K, S, Cl and Si contents. Soot consists of chain-like agglomerates of primary particles (10 – 100 nm) with a typical onion shell microstructure (graphene sheet separation distance between 0.133 and 0.137 nm). As our particles do not show the characteristics of all types of carbonaceous BB particles described above, this source can be excluded.

The most probable potential sources for carbonaceous particles were already discussed above. For these sources the transport mechanisms into the stratosphere are well known. There are further strong tropospheric sources for carbonaceous particles, which predominately emit particles at ground level. An effective transport to the stratosphere of these particles is unlikely. Still, they will be discussed briefly, as they are – on a global scale – major sources of carbonaceous material in the lower atmosphere.

Wood burning

Soot is a major component emitted by wood burning. Similar to biomass burning, soot from wood burning consists of agglomerates of spherical primary particles (20 – 80 nm diameter) with an onion-shell nanostructure (Kocbach et al., 2005; Torvela et al., 2014, Tumolva et al., 2010). Some primary particles are amorphous (Tumolva et al., 2010). The particles may have a surface coating which is volatile under electron bombardment (Torvela et al., 2014). Carbon is the major element of wood burning soot, O, Na, Si, S, Cl, K, and Ca occur as minor elements (Kocbach et al., 2005; Tumolva et al., 2010). In addition to soot, particulate organic matter (POM) was found in wood burning (Torvela et al., 2014). The POM particles, sometimes described as tar balls are 30 - 600 nm in diameter. Judged from the properties described above, both soot and POM are different to the particles observed in our study. Thus, wood burning can be excluded as a source for the refractory carbonaceous stratospheric particles.

Coal burning

A variety of different carbonaceous particles was observed during coal burning. Most carbonaceous particles are soot particles, i.e., fractal-like agglomerates (0.1 – 1 μm size) consisting of 10 – 50 nm diameter primary particles. The primary particles show a characteristic onion-shell structure (Chen et al., 2004, 2005). Some of the soot agglomerates have inorganic inclusions or inorganic particles on their surface, containing Mg, Ca, Sr (strontium), Ba (barium) and Na (Chen et al., 2005). Char particles associated with ultrafine titanium oxide particles were also found (Chen et al., 2005). Sometimes ultrafine Ti, Al, Fe and Ca particles were embedded in large char particles. In addition, graphitic fiber structures that are either straight or curved were encountered. Two of the three types of carbonaceous particles described for coal combustion (soot agglomerates and graphitic fibers) are certainly different from our particles. As images of char particles were not provided by Chen et al. (2005) we cannot compare their results to the refractory carbonaceous particles of the present study. **However**, we regard coal combustion as an implausible source.

Diesel engines

Diesel engines are another important source of carbonaceous particles and above all soot particles. Again, soot agglomerates consist of spherical primary particles (5 – 50 nm diameter) with onion-shell nanostructure (e.g., Tumolva et al., 2010; Wentzel et al., 2010; Li et al., 2011; Song, 2004; Weinbruch et al., 2016). The graphene sheet separation distance varies between 0.31 – 0.48 nm; (Vander Wal et al., 2010; Li et al., 2011; Weinbruch et al., 2016), and the intensity O/C ratio between 0.049 – 0.079 (Weinbruch et al., 2016). Compared to our particles, the chemical composition, morphology and primary particle size of diesel exhaust particles are significantly different. Thus, we can certainly exclude this source.

Ship emissions

Ship emissions also contain soot agglomerates (Popovicheva et al., 2012; Lieke et al., 2013). Their chemical composition is dominated by C and O, with small amounts (< 1 wt %) of additional elements; e.g. V, S, Cl, Ca and Si (Popovicheva et al., 2012). Furthermore, spherical char particles with diameters of 0.2 – 1 μm are found to be characteristic for ship emissions (Popovicheva et al., 2012). The morphology of these particles shown in SEM photomicrographs is different to the particles found in our study. Lieke et al., 2013 found amorphous carbonaceous material filling cavities of larger soot aggregates. The characteristics described for ship exhaust particles are

significantly different to the particles found in our study, leading to the conclusion that that ship exhaust can be excluded as the source.

5. Summary

The major finding of the present study is that the refractory component consists of carbonaceous particles only, with a number mixing ratio of $1.1 \text{ (mg air)}^{-1}$ (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 N_2O 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 burning, 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.

Data availability. The data set is available for the community and can be accessed by request to Katharina Schütze (schuetze@geo.tu-darmstadt.de) of the Technische Universität Darmstadt.

Author contributions. Katharina Schütze analyzed the samples, interpreted the data and prepared the manuscript. Nathalie Benker supported the TEM analysis. Martin Ebert came up with suggestions for and supported the SEM analysis. Stephan Weinbruch contributed to the preparation of the manuscript as well as interpretation and data analysis. Stephan Borrmann and Ralf Weigel supported the scope of the analysis as well as interpretation of data and writing. James C. Wilson provided the samples as well as any necessary data regarding the sampling campaign, contributed to the data analysis, interpretation and writing. Gebhard Günther conducted calculations on the meteorological situation of the collected samples.

Competing interests. All authors declare that they have no conflict of interest.

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Table 1: Sampling conditions

Table 1: Sampling conditions date (y/m/d/no)	sample In Vortex Out of Vortex	characteristics of flight* / Nitrogen Containing PSCs sampled	PV at Θ [PVU]	altitude [km] pressure [hPa] potential temperature Θ [K] #	CPC Aerosol Number Mixing Ratio, Number per milligram of air (mg air) ⁻¹	N ₂ O, Age of Air
2000-01-20_07	A In Vortex	PSC survey§/ PSCs sampled	26.2	19.7/ 57/ 433	Not available	165 ppbv 4.3 years
2000-01-20_11	B In Vortex	PSC survey§/ PSCs sampled	26.6	19.4/ 60/ 431	Not available	171 ppbv 4.2 years
2000-01-23_18	C In Vortex	vortex, sunrise / PSCs sampled	31.3	19.8/ 56/ 438	87	153 ppbv 4.5 years
2000-01-27_15	D Out of Vortex	edge survey / No PSCs	24.7	19.9/ 56/ 448	72	227 ppbv 3.6 years
2000-01-31_18	E In Vortex	vortex survey/ PSCs sampled	32.0	19.7/ 59/ 437	88	171 ppbv 4.2 years
2000-02-02_19	F In Vortex	vortex survey/ PSC Unknown/	26.5	18.6/ 68/ 425	86	167 ppbv 4.3 years
2000-02-03_15	G In Vortex	multiple level/ PSCs sampled/	18.2	17.4/ 83/ 400	65	209 ppbv 3.7 years
2000-02-26_12	H In Vortex	vortex survey/ No PSCs	30.3	19.1/ 62/ 430	87	143 ppbv 4.6 years
2000-02-26_14	I In Vortex	vortex survey/ No PSC s	30.4	17.3/ 64/ 431	90	137 ppbv 4.7 years
2000-03-05_19	J In Vortex	vortex survey PSC unknown	27.7	19.2/ 64/ 424	63	150 ppbv 4.5 years
2000-03-11_19	K In vortex	vortex edge PSCs unknown	29.6	18.7/ 66/ 430	89	136 ppbv 4.7 years

* according to Newman et al. (2002), # during sampling, § no particles out of PSCs were analyzed; PV= Potential Vorticity, PVU= Potential Vorticity Unit [10^{-6} K m² kg⁻¹ s⁻¹]

Table 2: Overview over particle parameters investigated.

Information	Number of particles investigated	Applied in Figure/Table	Method
Size, morphology, chemical composition	529	Figure 3	TEM
Mixing state, morphology	3316	---	
Nanostructure	23	Table 4, Figure 7	
Distribution of elements within the particles	4	Figure 5	STEM
Size, morphology, chemical composition	330	Figure 3, Figure 4, Figure 6, Figure 8	SEM
Sum of total particles	4202		

Table 3: Absolute number of refractory particles as function of particle group.

Particle group	sample										
	A	B	C	D	E	F	G	H	I	J	K
C, O, Si	4	8	3	2	4	8	11	3	4	3	2
+ Cr, Fe, Ni	15	6	15	10	14	9	3	12	14	21	12
+ Cr, Fe	10	13	12	13	12	9	11	13	12	4	16
+ Fe	1	3	0	5	0	4	5	2	0	2	0

Table 4: Graphene sheet separation distance

Particle [#]	Separation distance [nm]		
	mean value	minimum - maximum	n
A-1	0.38	0.35 – 0.39	3
B-1	0.35	0.23 – 0.45	10
C-1	0.35	0.33 – 0.37	5
C-2	0.39	0.35 – 0.45	4
C-3	0.41	0.37 – 0.48	5
C-4	0.37	0.32 – 0.42	4
C-5	0.38	0.34 – 0.40	6
C-6	0.39	0.33 – 0.47	5
C-7	0.38	0.35 – 0.40	5
G-1	0.42	0.34 – 0.51	14
G-2	0.47	0.37 – 0.60	18
G-3	0.42	0.38 – 0.49	15
G-4	0.43	0.40 – 0.53	35
G-5	0.43	0.36 – 0.51	20
G-6	0.29	0.19 – 0.32	25
G-7	0.43	0.38 – 0.51	20
I-1	0.34	0.31 – 0.39	4
I-2	0.27	0.24 – 0.29	4
I-3	0.27	0.25 – 0.28	3
I-4	0.25	0.23 – 0.26	3
I-5	0.46	0.44 – 0.48	3
I-6	0.30	0.28 – 0.33	4
I-7	0.33	0.32 – 0.34	3

[#]sample-particle

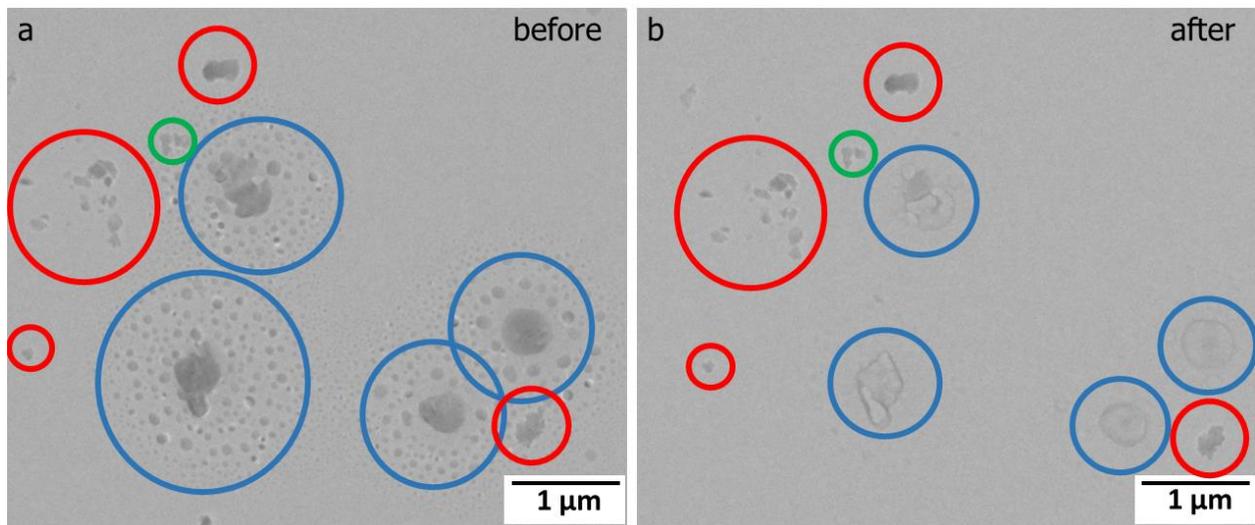
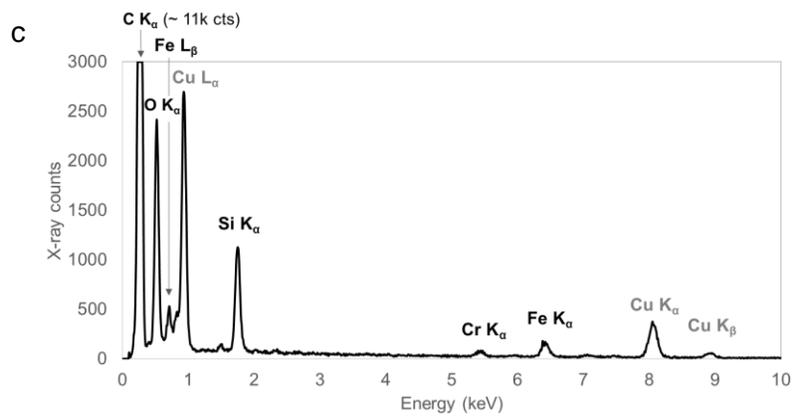
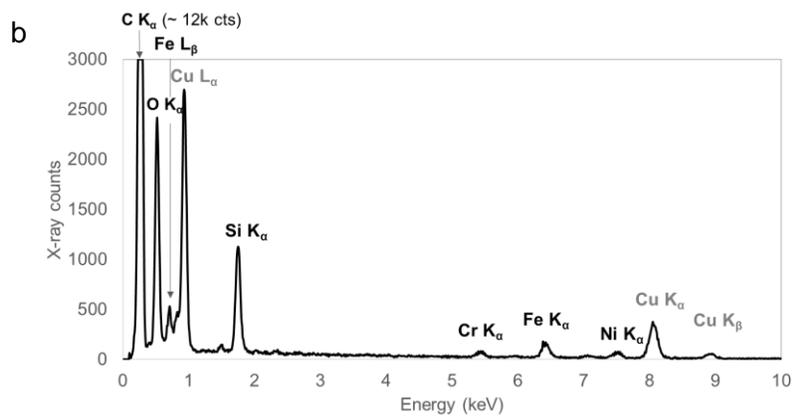
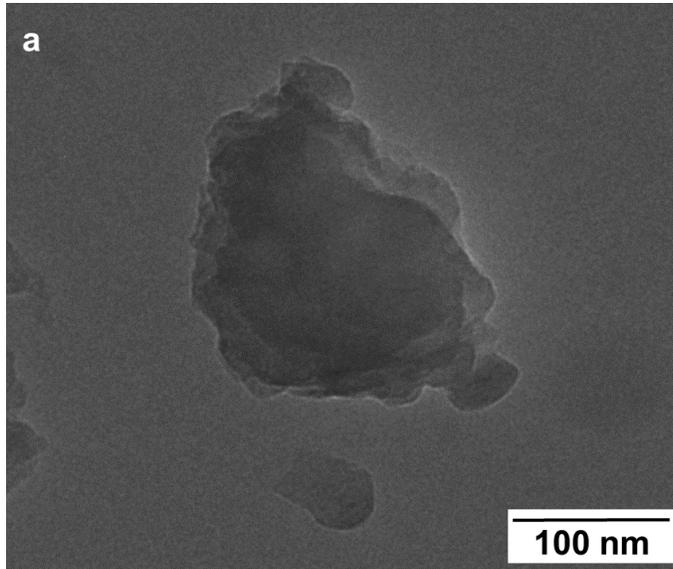
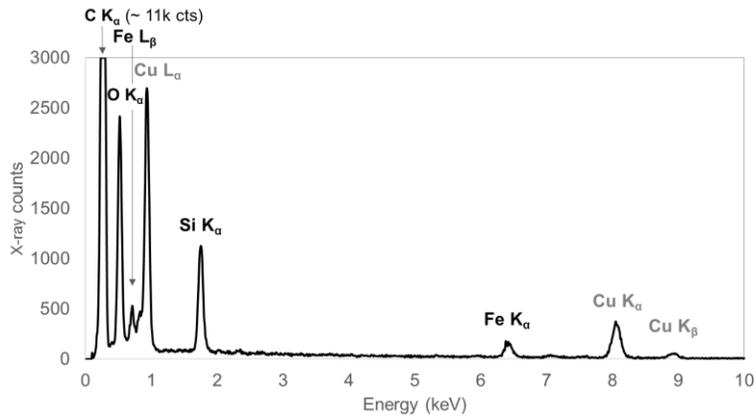


Figure 1: TEM bright field image of a typical sample (sample I; 17.3 km altitude), before (a) and after evaporation (b). Particles evaporating under electron bombardment are marked with blue circles. They consist of sulfates/hydrogen sulfates. Red circles indicate stable carbonaceous particles. Green circles show refractory carbonaceous particle internally mixed with volatile sulfates/hydrogen sulfates.



d



e

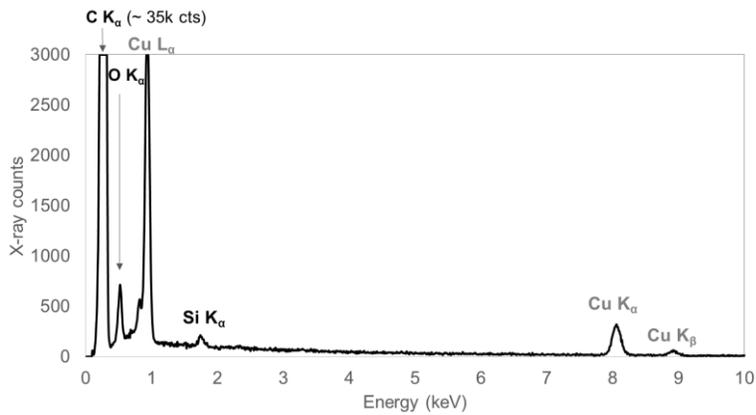


Figure 2: TEM bright field image (a) of a typical refractory carbonaceous particle from sample H (19.1 km altitude). The image is representative for all refractory carbonaceous particles. The morphology is not depending on chemical composition, size, morphology or nanostructure. Energy-dispersive X-ray 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. K α and K β as well as L α and L β denote different X-ray peaks emitted from the same element.

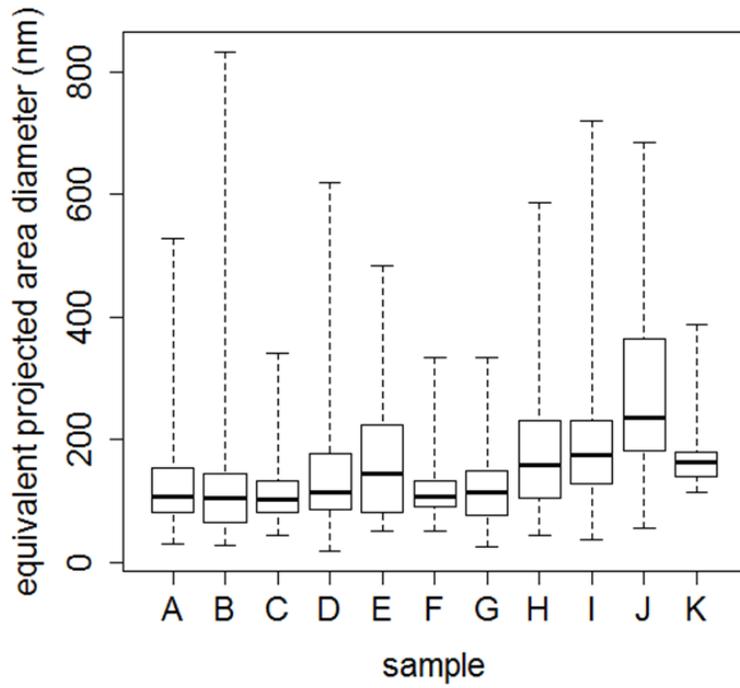


Figure 3: Boxplot of particle size (equivalent projected area diameter D_{pa}). Lower and upper quartiles appear as a box, minimum and maximum values as whiskers.

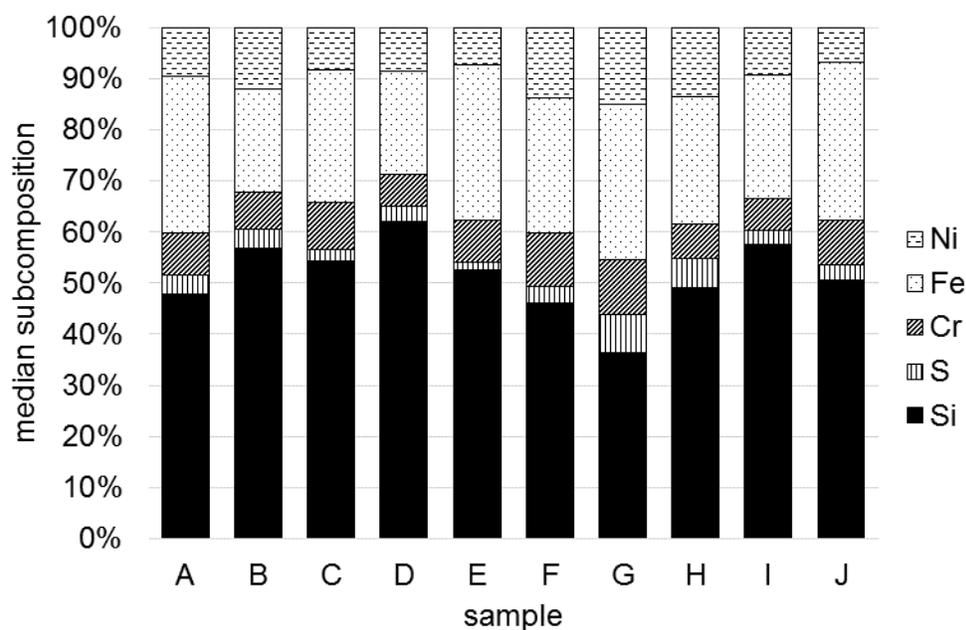


Figure 4: Median chemical subcomposition (atom %, without C and O) of refractory carbonaceous particles determined by SEM-EDX (30 particles per sample). Sample K was excluded from the figure due to a different substrate with higher Si content.

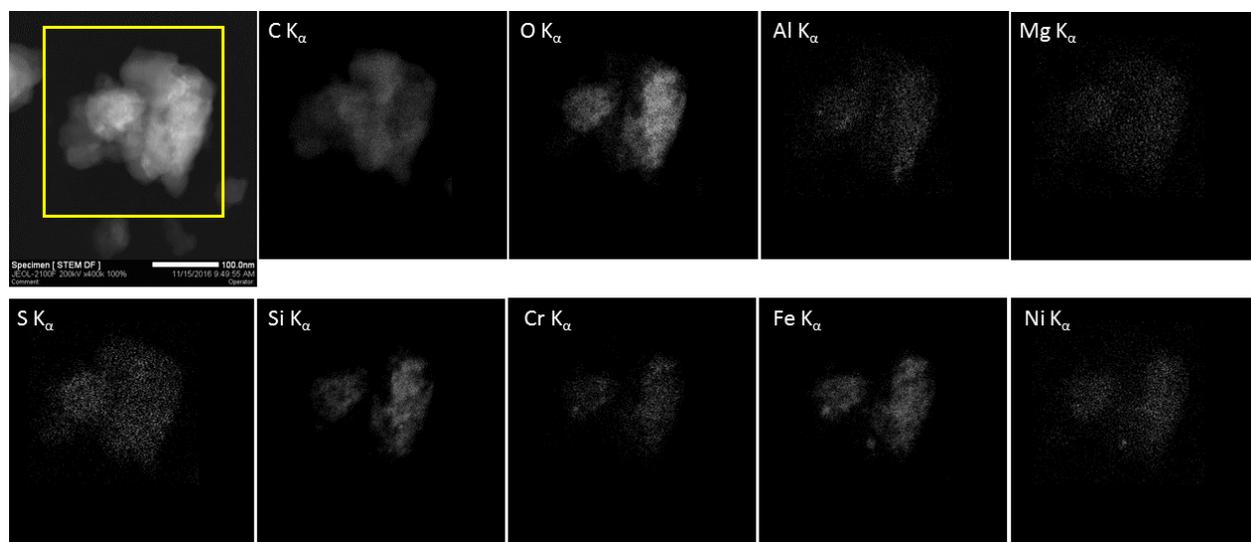


Figure 5: STEM image (upper left) and element distribution images of a refractory carbonaceous particle from sample C (19.8 km altitude).

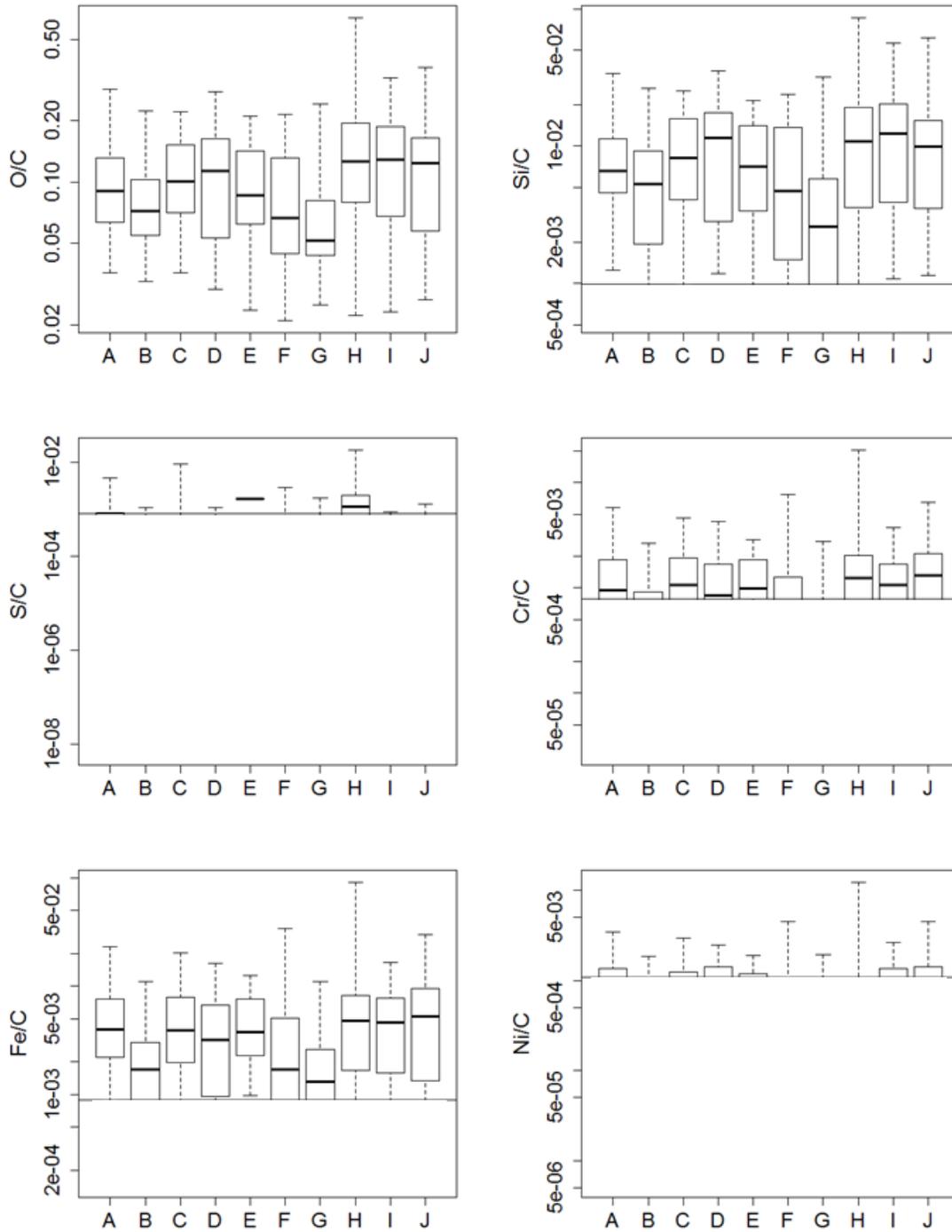


Figure 6: Censored boxplots of element ratios relative to C (atom %) determined by SEM-EDX (30 particles per sample). Sample K is not shown due to the different substrate used. Lower and upper quartiles appear as a box, minimum and maximum values as whiskers. Values below detection limit (horizontal line) are not shown.

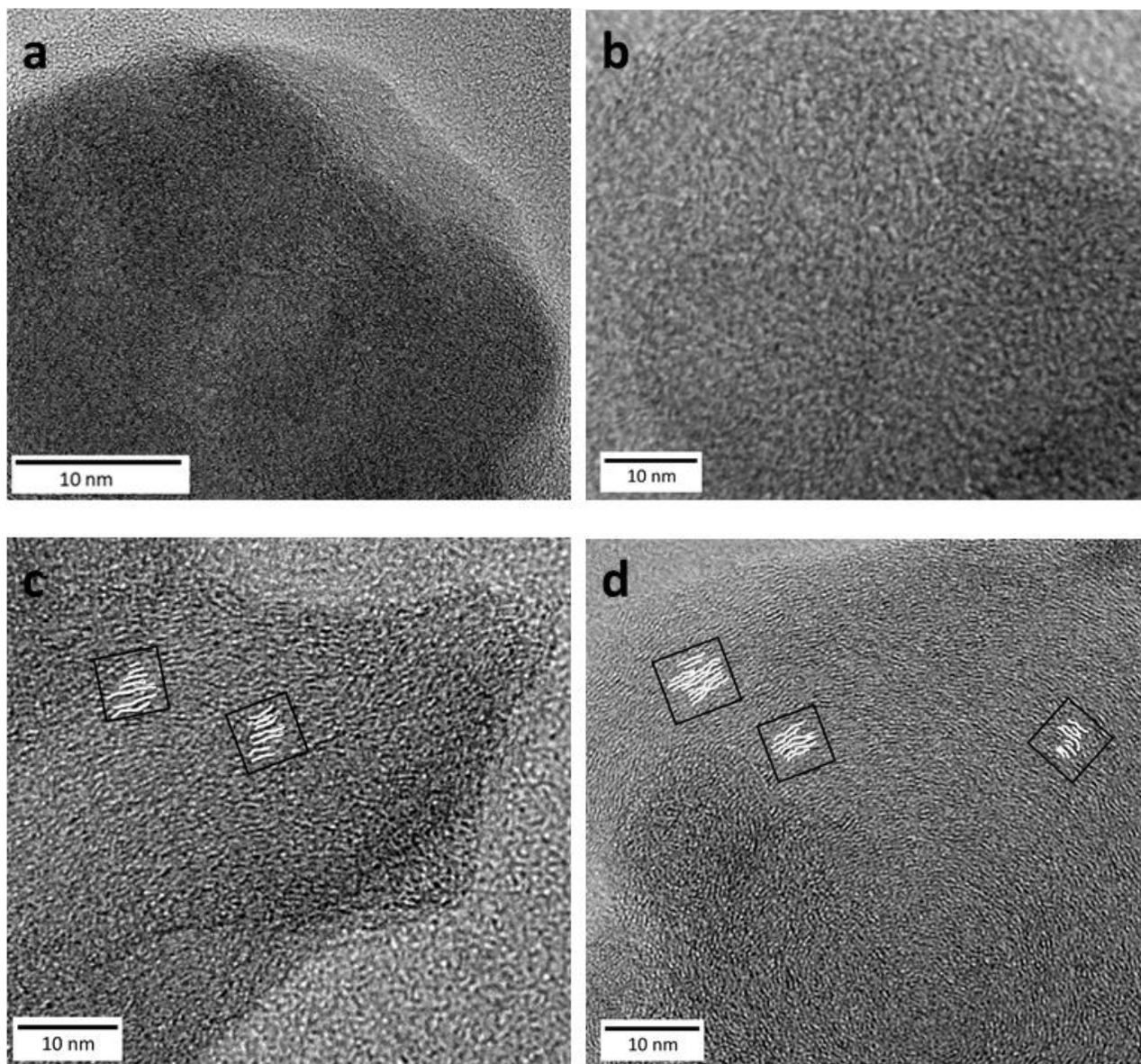


Figure 7: High resolution TEM image of individual refractory carbonaceous particles from sample G (17.4 km altitude): (a, b) completely amorphous particles, (c, d) particles showing small regions with ordering.

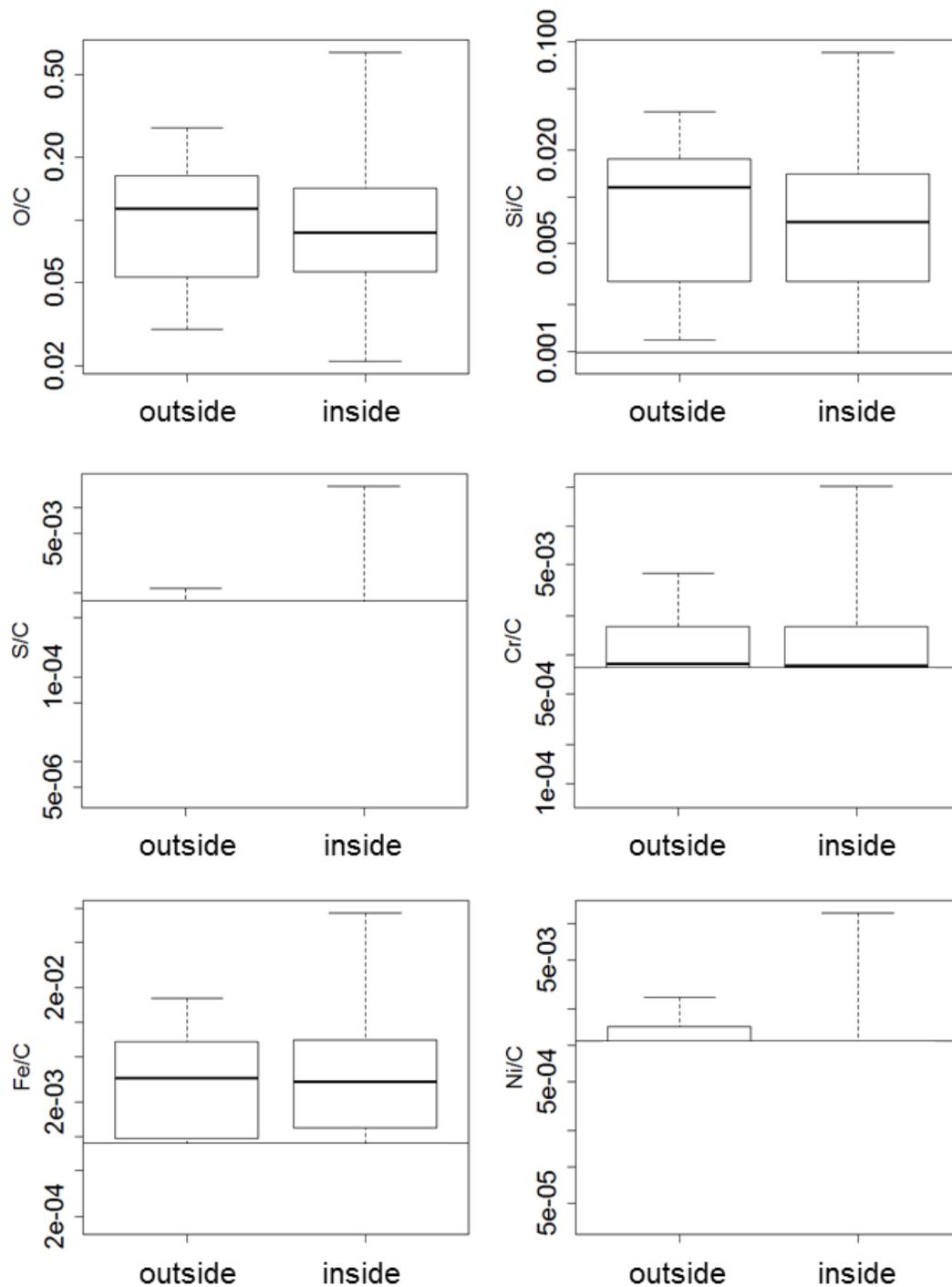


Figure 8: Censored boxplots of element ratios (atom %) relative to C, separately for outside and inside the polar vortex. Sample K was excluded from the analysis due to the different substrate used. Lower and upper quartiles appear as a box, minimum and maximum values as whiskers. Values below detection limit (horizontal line) are not shown.