

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

### **Anonymous Referee #1**

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Review of Schuetze et al.

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.

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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.

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.

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?

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 H<sub>2</sub>SO<sub>4</sub> 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 H<sub>2</sub>SO<sub>4</sub> 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.

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

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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.

c) Neither rocket exhaust nor extraterrestrial material are very consistent with the data. Kerosene rockets should produce soot, which was not observed. It is also doubtful that there are enough particulate emissions from non-solid-fuel rocket exhaust in the upper stratosphere to account for the observed particles. Note that the authors measured more carbonaceous material than meteor smoke. The authors could compare the estimated particulate emissions from rockets to the extraterrestrial flux to see if it is plausible that there is more carbonaceous material from rockets than meteoric smoke in the polar stratosphere. I tried a quick estimate and I don't think there is enough exhaust compared to meteor smoke, but I didn't spend much time tracking down references.

Considering extraterrestrial material, there is too little Mg, Si, and Fe compared to carbon. For example, the carbon to silicon atomic ratio in micrometeorites collected in the stratosphere is about 1.3 to 2.4, (Shramm et al., 1989) but in these data it is over 30 (Figure 9). Even "carbonaceous" meteorites have more Mg, Si, and Fe than observed in these particles. In addition, the carbon in a meteoroid that got hot would oxidize to CO<sub>2</sub> 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.

3) Minor comments.

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

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

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suggest that the authors consider secondary organic material more seriously, either formed in the troposphere or stratosphere.

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

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.

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 N<sub>2</sub>O was measured during SOLVE.

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

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

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