Atmos. Chem. Phys. Discuss.,
https://doi.org/10.5194/acp-2017-278-AC3, 2017

Atmospheric Chemistry and Physics
Discussions

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

Katharina Schütze et al.

schuetze@geo.tu-darmstadt.de

Received and published: 30 August 2017

We gratefully acknowledge the suggestions of Alexander D. James and included them to the revised version of the paper. We believe that the changes considerably helped to improve the quality of the manuscript.

This article has the potential to be a useful addition to the understanding of stratospheric aerosol, particularly since there are relatively few capture and return samples with statistics on this level. Whilst the conclusions they are able to draw are limited, publication of such data is vital in facilitating future understanding. I feel that the authors have missed or omitted a section of the literature which, once considered, can both add to the understanding of the results and increase the potential audience of the

article. Below are a number of specific comments on language, formatting and content. The authors provide a good introduction to the current and historical field. I was surprised to see no reference to the recent and thorough review of Kremser et al. (2016), who summarised some of the studies mentioned in the introduction of this work and other related topics.

We have mentioned the publication of Kremser et al. (2016) lateron at the beginning of chapter 3. But we agree that the mentioned paper is a very good recent summary of past findings and therefore decided to add the following sentence to the end of the first paragraph of the introduction: "A comprehensive summary of stratospheric aerosol and sulfur chemistry is given by Kremser et al. (2016)."

Page 4 line 2; change "extend" to read "extent".

Accordingly changed.

The analysis of images for structure of carbonaceous material is interesting. Was electron diffraction data recorded for any samples?

Unfortunately it was not possible to conduct electron diffraction with the samples.

Page 5 line 8; reformat 5 $\times$ 10-3.

Accordingly changed.

Page 5 line 27; amend to "too close to"

Accordingly changed.

Page 5 line 30 onwards; sentence is hard to understand. Perhaps "Any particle which showed no signs of destruction or morphological change was taken to be non-volatile. Particles which changed under the electron beam were deemed volatile, allowing quantification of the fraction of aerosol which is volatile."

We have removed the whole paragraph.

Section 4.1; I believe this section would benefit from also discussing the size ranges of the various particles. For example Ebert et al. (2016) discuss mainly particles of radius greater than 500 nm, which have metallic or meteoritic composition. In that study the smaller size fraction is described as being largely carbonaceous material in sulfate liquid droplets, similar to the findings of this study.

We added the size ranges of the particles described in that section in arrows: Blake and Kato (1995): $\leq$ 0.5 nm; Pueschel et al. (1992): $\sim$0.2 – 0.3 μm; Pueschel et al. (1997): $\leq$ 1um; Sheridan et al. (1994): $\sim$ 0.3 μm; Strawa et al. (1999): $\sim$0.3 - 0.4 μm; Chuan and Woods (1984): $\sim$0.1 μm; Ebert et al. (2016): $\leq$ 0.500 μm; Chen et al. (1998): $\leq$ 0.1 - 2 μm; Nguyen et al., 2008: $\leq$ 1 μm; Baumgardner et al. (2004): 0.15 - 1 μm; Schwarz et al. (2006): 0.15 - 0.7 μm; Renard et al. (2008): 0.35 - 2 μm

Page 12 line 1; change to "the particles described above matches the refractory. . ."

Accordingly changed.

Possibility that particles have an extraterrestrial origin; this section makes a good comparison between measurements of extraterrestrial material and the particles observed in the stratosphere. What is lacking is any discussion of the process which occur as a result of frictional heating during atmospheric entry. There is currently some discussion of whether unablated meteoric material will sediment too rapidly to be found in the stratosphere (Carrillo-Sánchez et al., 2016), or whether significant fragmentation of ablating meteorites could lead to smaller aerosol with longer atmospheric lifetimes (Subasinghe et al., 2016). Considering these processes in the light of the results presented here would broaden the appeal of the current results to a wider audience and add significantly to the conclusions the authors are able to draw from their data. Regarding ablation: The fact that the three metals discussed; Ni, Fe and Cr; have ratios significantly different than their chondritic abundances has rather more interesting implications when considered with respect to the ablation process. Since in interplanetary dust Ni is largely contained in relatively volatile metal phases (melting points

around 1200-1500 K), Fe is spread between volatile metallic and more refractory silicate phases (melting point >1800 K) and Cr is contained in the less volatile silicates (Bunch and Olsen, 1975), the three elements will ablate rather differently (Gómez-Martín et al., 2017). The relative volatility of Ni is therefore reconcilable with the larger Ni/Fe ratio measured here and does not rule out an extraterrestrial source, but the high Cr/Fe and Cr/Ni suggest that Cr at least has a terrestrial source, since if anything Cr should ablate less completely than the other elements. Regarding fragmentation: This is hypothesized to happen by evaporation of volatile phases such as iron sulfides and amorphous carbonaceous material (ordered graphitic material would be much more refractory). It may be reasonable as a result that the metal bearing silicates would remain in larger particles which have very short lifetimes in the stratosphere, but carbonaceous material and some additional Fe is atmospherically available as a result. The question could possibly be more constructively phrased in another way. Since we know that meteoric ablation occurs and meteoric smoke forms, why is it not unequivocally observed in these measurements? Indeed numerical modelling of MSPs suggests that they should be observable in this size range (Bardeen et al., 2008). Could it be that nucleation, growth and sedimentation of crystalline PSC has removed meteoric material? What implications would the partial dissolution of metals have on these measurements? Could dissolution, precipitation and agglomeration in liquid droplets cause more rapid growth of MSP compared to model predictions?

We highly appreciate this comment! Considering the given comment and included literature, we included the suggestions into the paper. Now, we added the following paragraph to the "extraterrestrial particles" section in 4.2: "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." In addition, we added to the abstract: "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.", and to the summary: "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." These comments also inherently include the issue of sample aging, which both anonymous reviewers rightly mention. Having some experience of electron microscopy, I suspect that this statistical detail could only be reached from measurements which would take several years to make. In addition to the reviewer's comments then, the possibility should be considered that some samples have aged more than others.

According to this comment we added the following sentence at the end of chapter 2.1: "Anyhow, it should be kept in mind that other parameters (chemical composition, mixing state) may be changed to a variable extent by aging."

References Bardeen, C. G., Toon, O. B., Jensen, E. J., Marsh, D. R., and Harvey, V. L.: Numerical simulations of the three-dimensional distribution of meteoric dust in

the mesosphere and upper stratosphere, J. Geophys. Res.: Atmos., 113, D17202, 2008. Bunch, T. E., and Olsen, E.: Distribution and significance of chromium in meteorites, Geochim. Cosmochim. Acta, 39, 911-927, http://dx.doi.org/10.1016/0016-7037(75)90037-X, 1975. Carrillo-Sánchez, J. D., NesvornÃ¡, D., PokornÃ¡, P., Janches, D., and Plane, J. M. C.: Sources of cosmic dust in the Earth's atmosphere, Geophys. Res. Lett., 43, 11,979- 911,986, 10.1002/2016GL071697, 2016. Ebert, M., Weigel, R., Kandler, K., Günther, G., Molleker, S., Grooß, J. U., Vogel, B., Weinbruch, S., and Borrmann, S.: Chemical analysis of refractory stratospheric aerosol particles collected within the arctic vortex and inside polar stratospheric clouds, Atmos. Chem. Phys., 16, 8405-8421, 2016. Gómez-Martín, J. C., Bones, D. L., Carrillo-Sánchez, J. D., James, A. D., Trigo- Rodríguez, J. M., B. Fegley, J., and Plane, J. M. C.: Novel experimental simulations of the atmospheric injection of meteoric metals, Astrophys. J., 836, 212, 2017. Kremser, S., Thomason, L. W., von Hobe, M., Hermann, M., Deshler, T., Timmreck, C., Toohey, M., Stenke, A., Schwarz, J. P., Weigel, R., Fueglistaler, S., Prata, F. J., Vernier, J. P., Schlager, H., Barnes, J. E., Antuña-Marrero, J.-C., Fairlie, D., Palm, M., Mahieu, E., Notholt, J., Rex, M., Bingen, C., Vanhellemont, F., Bourassa, A., Plane, J. M. C., Klocke, D., Carn, S. A., Clarisse, L., Trickl, T., Neely, R., James, A. D., Rieger, L., Wilson, J. C., and Meland, B.: Stratospheric aerosolâĂŤObservations, processes, and impact on climate, Rev. Geophys., 54, 278-335, 2016. Subasinghe, D., Campbell-Brown, M. D., and Stokan, E.: Physical characteristics of faint meteors by light curve and high-resolution observations, and the implications for parent bodies, Mon. Not. Royal Astro. Soc., 457, 1289-1298, 2016.

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