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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Thermal stability analysis of particles incorporated in cirrus crystals and of non-activated particles in between the cirrus crystals: Comparing clean and polluted air masses" *by* M. Seifert et al.

M. Seifert et al.

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Special comments:

1. a) Stainless steel artifacts

Reviewer: "Unfortunately, this manuscript suffers several critical flaws. Specifically, artifacts associated with the sampling of atmospheric ice crystals are not described and it is very likely they corrupt the quality of the presented data rendering the conclusions which the authors draw false. "

"I believe that it is likely that the CVI employed by the authors is susceptible to the liberation of sub-micron metal particles (non-volatile) when ice crystals are sampled. Please see the presentation at: http://cloud1.arc.nasa.gov/crystalface/postpresentations.html (see “Sampling in Ice Clouds ”) which describes this process. ”

“ I am left to conclude that the most likely reason for the authorsŠ observations is the production of non-volatile material within their own instrument and not an atmospheric phenomenon. The mechanism has been shown to occur by other researchers. The authors attempts to explain their observations are either incorrect or pure speculation. ”

Reply: The reviewer makes some rather strong and clear statements about what he/she believes is the origin of the non-volatile particles (at 250 °C) presented in this study. Unfortunately, the reviewer provides no suggestions for how this would come about other then referring to a presentation by Murphy et al. that is available on the internet.

One of the authors (Johan Ström) was contacted by Dan Murphy during fall of 2002 where he gave some information about his findings and shared his ideas about the possibility that crystals would be able to remove pieces of stainless steel from the sampling inlet. This initial contact was followed by a short exchange of thoughts and ideas via e-mail. Although the findings by Murphy et al. are interesting and to some extent puzzling, the available data does not warrant the conclusions made by the reviewer.

Below we will address this issue, using what we think is relevant information.

The fundamental assumption when studying residual particles sampled by the CVI is the one-to-one relation between the number of hydrometeors sampled and the number of residual particles observed. In many of the 100+ references dealing with CVI data and its operation (compiled by John Ogren and listed at http://www.cmdl.noaa.gov/aero/pubs/cvi.html) potential problems such as shattering of crystals have repeatedly been addressed because the reviewer did not believe in the results.

The two INCA campaigns provided a rather extensive data set (in comparison to other aircraft in-situ campaigns) of concurrent measurements by the FSSP-300 and the CVI in very different environments. In Seifert et al. (2003) we compared the ice particle concentration obtained from the CVI (NCVI) and the FSSP 300 (NFSSP) based on more than 20 hours of in-cloud-data. A lower size limit of 4 μm was chosen for the FSSP-300 data since it gave the best agreement between the two instruments. The resulting data has been classified according to Ncvi into bins. A very good agreement between NFSSP and NCVI at crystal number densities was found between 0.1 and 5 cm-3. At lower number densities NFSSP is nearly constant which is simply a result of the detection limit of the FSSP-300, corresponding to one count during the sampling time interval. Over several orders in magnitude the two instruments agree very well along the one-to-one line. Hence the CVI-FSSP-comparison presented in Seifert et al. (2003) clearly show that the number density of residual particles observed by the CVI correspond to the number density of hydrometeors observed by the FSSP-300. Note that the corresponding plot refers to figure 1 on the following webside: www.itm.su.se/dokument/acpreview.html

With reference to the issue of crystals taking chunks of metals from the sampling device, the one-to-one relation between NFSSP and NCVI found in Seifert et al. (2003) provides us with three options. A. Each crystal leaves only one residual particle and no other particles are produced by potential impacts. B. No crystal leaves any residual particles, but all crystals impact and generate one artifact particle each. C. A combination of A and B. However, C can not just be any combination. Due to the obviously strong agreement between the two devices it would preferably be crystals that do not leave any residual particles that also generate artifact particles by impaction, or there would not be a one-to-one relation between the FSSP-300 and the CVI. One other possibility would be some sort of proportionality relation between crystals that leave a residual particle, those that dont, and those that generate artifact particles, such that the sum always is equal to the integral observed by the FSSP-300.

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Because the reviewer bases so much of his/her conclusions on the content in the presentation by Murphy et al. (2003) we feel it necessary to repeatedly refer to this presentation in our response. We feel a little uneasy towards this since it renders something of a review of a presentation, which is not really fair to Murphy et al. who have had to omit important information in the interest of making a time limited presentation. Nevertheless, it is the information referred to by the reviewer and thus part of arguments used by the reviewer.

In their presentation Murphy et al. (2003) states that ca. 90% of the residual particle spectra contained metal (D>0.2 μm diameter). Statistics over the particle types are not presented, but examples of typical metal spectra are provided. What fraction of these metal particles is actually classified as stainless steal is not mentioned. Based on the observation that metal particles are unambiguously correlated with the presence of ice or dust and that the observations suggests a very large source of metals to the free troposphere, Murphy et al. concluded that:

- Ice crystals can knock pre-existing particles off the wall of an inlet. Ice crystals appear to be able to abrade stainless steel.

- Some real metal particles are possible. However, to explain published CVI data the global flux would be very substantial.

- Abrasion/shattering may be frequent enough to affect data on ice number, especially if knocking older particles off the wall. Water content should be ok.

In support of their conclusions Murphy et al. refer to other studies where metal signatures have been observed in residual particles.

We have tried to compile available data to illustrate what the discussion is about. The data are single particle analysis made on filter/impactor samples collected downstream of various CVI probes. There are two sets of data from the INCA experiment (unpublished and preliminary). Both campaigns are represented, but the data sets are analyzed at different labs using different coatings. The SH samples were coated with silver and analyzed at the Technical University of Munich by the group of Dr. Ulrich Pöschl. The NH samples were coated with carbon and analyzed by our group. The other studies used here are Heintzenberg et al. (1996), Twohy and Gandrud (1998), and Twohy et al. (2003).

Based on our INCA data we divided the particles into five groups for which the respective fraction was calculated. The five groups are:

1. Particles containing Fe 2. Particles containing Fe and Cr 3. Particles containing Fe and Cr, but no Si 4. Particles containing Fe and Cr, but no Si, S, Cl, Na, or Al 5. Particles containing Fe, Cr and Ni, but no Si, S, Cl, Na, or Al

From Heintzenberg et al. (1996) the data can be grouped as was done for the INCA data. The data from Twohy and Gandrud (1998) and Twohy et al. (2003) had to be arranged differently, but the grouping was done in such a way that the result probably came very close to the grouping used for the other data sets.

Plotting the fraction of particles that contain Fe shows that the residual particles may be dominated by types containing Fe. In group 1 the fraction varies between about 30-70% for different studies. However, as we change the particles types to be more and more close to pure stainless steel, the fraction drops rapidly: group 2 (about 10-30%), group 3 (about 5-20%), group 4 (about 5-15%) and group 5 (<5%). Note that the corresponding plot refers to figure 2 on the following webside: www.itm.su.se/dokument/acpreview.html

It is very difficult to understand how stainless steel particles would mix with any other material during the impact by the crystal. Therefore, particles with metal signature mixed with anything else than trace amounts of Si, Na, Ca, Al etc. are not likely a product of crystal impact. When introducing increasingly stringent conditions for what is called a stainless particle the fraction of possible stainless steel particles is reduced to on the order of 10%. In terms of the INCA data, which is on review here, this fraction

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is less than 5%. The Petzold et al. (1998) study did not present the data in a way that it can be compared with the other studies. Nevertheless, the study states that the metal particles found are clearly associated with the larger particles. We note also in their figure 1 (comparing interstitial and residual size distributions) that the residuals by no means make up all the available particles in the interstitial air in the size range of the observations. We will return to this below.

The NH-data is given as relative abundance and we may study the fraction of particles that contain Fe in a different way for comparison. Our data is divided into four groups:

1. Particles containing Fe
2. Particles containing at least 50% Fe
3. Particles containing at least 50% Fe and detectable amounts of Cr
4. Particles containing at least 50% Fe and detectable amounts of Cr but no Si

Note that the corresponding plot refers to figure 3 on the following website: www.itm.su.se/dokument/acpreview.html. The fraction of particles containing Fe is about 30% (group 1). Particles which at least have an abundance of 50% Fe, stand for about 10% (group 2). Including the additional requirement that Cr must also be present, causes the fraction of Fe containing particles to drop to about 5% (group 3). Finally, in group 4 where iron particles may not contain any detectable amounts of Si we find an abundance of less than 2.5%. As for the criterion used before we find a similar trend although slightly different criteria are used. In essence the observations suggest that a few percent of the residual particles larger than approximately 0.1 μm in diameter may be a result of crystal impactions. This assumes that none of these particles arrived on the filter as contamination during handling of the specimen.

As pointed out by the reviewer metal particles have been observed previously in the upper troposphere Sheridan et al. (1994). During the INSTAC campaign 1989 over the tropics in the southern hemisphere, mineral particles containing Fe-Cr-Ni were observed in the upper troposphere by Kikuo Okada (personal communication). The data (not collected using a CVI) was presented at a Japan Meteorological Society meeting. Due to the similarities to stainless steel, Kikuo Okada choose not to write a scientific report in a peer-reviewed Journal about his findings.

Murphy et al. (2003) also notes that the chemical signature of the stainless steel particles do not always match the inlet material. Using INCA NH-data again we can generate a ternary diagram for Fe, Cr, and Ni. Because these three elements do not always make up 100% of the particles we have simply normalized the contribution of the three elements to 100%. Note that the corresponding plot refers to figure 4 on the following webside: www.itm.su.se/dokument/acpreview.html. Furthermore material was taken from our probe (from the inlet as well as from the porous part of the tip) and put on the same type of substrate as used during the campaigns and analyzed on the same machine as the NH data. Several particles taken from the probe were analyzed and the variability was within a few percent. Comparing residual particles to particles from the probe shows that two particles are consistent with the porous material and three particles are close to but not quite consistent with the composition of the rest of the probe. Five stainless steel particles consistent with the composition of the probe in more than 300 particles analyzed give a fraction of less than 2%.

One argument for the artifact problem put forward by Murphy et al. (2003) is the observation that the metal particle fraction stays constant over a change in crystal number density ranging over more than four orders of magnitude. If this is actually in support of the idea about metal artifacts or not can be discussed. Depending on the mode of nucleation we except that different relationships between metal particles and ice crystals can be possible (this includes a constant factor). Our manuscript in review actually contains a figure that can be compared to the figure showing a constant fraction presented by Murphy et al. (2003). Figure 4 in the revised version of our manuscript shows the deviation from the average volatility fractions as a function of crystal number density. Leaving out normalization this plot is the equivalent to the plot in the presentation by

Murphy at al. (2003). Using this data we can highlight a few points. Plotting the non-volatile residual particles fractions as a function of Ncvi shows the data clearly different from a constant value. Note that the corresponding plot refers to figure 5 (middle column) on the following webside: www.itm.su.se/dokument/acpreview.html. The ratios differ between temperature ranges as well as between campaigns.

This variable behavior by the fraction is coupled to the discussion of the one-to-one relation between the number of residuals and crystals in the beginning of our reply. With a variable non-volatile particle fraction an exotic relation between the production of artifact particles and sampling of real residual particles is needed in order to result in the strong correlation between the FSSP-300 and the CVI total number densities. Plotting the absolute number of non-volatile residual and interstitial particles for the INCA data shows clearly that the ambient number densities of non-volatile particles always are much higher than the number densities of residual particles. Recall that this was also shown in the Petzold et al (1998) data. Note that the corresponding plot refers to figure 5 (right column) on the following webside: www.itm.su.se/dokument/acpreview.html.

Futhermore comparing the number of non-volatile particle as a function of crystal number density of the residuals to the interstitial aerosol highlights a very important fact: There are always more non-volatile particles available in the ambient air than is found in the crystal residuals. We emphasize that the interstitial and out-of-cloud data is collected using an inlet different from the CVI. This inlet is facing opposite to the flight direction. Thus impaction by large particles inside the probe is impossible. Although we can not say what these particles are composed of (see response to other comments by the reviewer) we know that they are present in the atmosphere and potentially available as ice nuclei. The reviewer makes no comment in reference to the interstitial and out-of-cloud data. However, based on the conclusions by the reviewer these data must also have been dismissed for one reason or the other.

One other very important fact is that: whereas the analysis by Murphy at al. (2003) only concerns particles larger than about 200 nm in diameter, the non-volatile residual

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particles observed by the CVI are controlled to 90% by particles smaller than about 100 nm. Thus, the conclusion by the reviewer that metal artifacts is the source of the non-volatile residual particles, based on the Murphy et al. (2003) presentation, can never be anything other than suggestive or pure speculations. The presentation by Twohy et al. (2003) (Crystal Face) summarize that large nuclei are more of metal and crustal dust types, and small nuclei are more organics and sulfate type particles. The INCA data also shows that metal type particles are predominantly associated with the larger particles (as did Petzold et al., 1998). To illustrate this, the residual particle composition is studied as function of size for the INCA SH-data. Note that the corresponding plot refers to figure 6 (right column) on the following webside: www.itm.su.se/dokument/acpreview.html.

The resulting data is rather different from the distribution presented by Murphy et al. (2003). One explanation for this is that they perhaps classify all particles containing Fe as metals. In our opinion it is the particles that may be classified as stainless steel that are relevant for the idea about metal artifacts from impacting crystals. Our data indicates that the fraction of stainless steel particles decreases with size, which suggests that any potential metal artifact problems would be less for small particles (i.e. particles smaller than the detection limit of PALMS). We emphasize that we donŠt know the properties of particles smaller than ca. 100 nm. The properties observed for particles larger than 100 nm may or may not be related to the properties of particles smaller than 100 nm.

There are clearly several differences in the observations presented by Murphy et al. (2003) and the results obtained by other groups analyzing the chemical composition of residual particles. If this is because Murphy et al. (2003) have a problem with metal artifacts due to impacting crystals or their PALMS instrument is more sensitive to metal particles than other devices is impossible to decide with the limited data at hands.

In our opinion there is nothing in the presentation by Murphy at al. (2003) or in our own data that warrant the conclusion that non-volatile particles are a result

of stainless steel particles being removed from the inlet by impacting crystals. To the contrary our data is not consistent with the potential problem proposed by the reviewer.

We have no firm suggestions for why the PALMS data is different from other results, and it would require an in-depth knowledge about details of their inlet system to propose a plausible process. For instance; what is the influence of the long shroud, are different groups using steel of different grades (hardness), are the ambient environments at the point of determining the elemental composition influencing the results etc.? We do however note a significant difference in the operation of the CVI between our group and the group of Dan Murphy. In the presentation by Murphy at al. (2003) they state that the CVI is used as an aerosol probe when the aircraft is out-of-cloud. Because the CVI is not a very good aerosol probe, but also because we want to keep our sampling lines clean, our CVI is always operated using the counterflow. On the ground the probe is covered immediately after the flight. If the CVI probe is used to aspirate ambient air there is a risk that air is going backwards and contaminates the porous part of the tip and the interior of the probe. To avoid potential problems we use different inlets for sampling ambient aerosols and ice crystals, which also allows us to get concurrent observations. More knowledge about the transfer efficiency of the PALMS instrument for accumulation mode particles might give some insight to the different metal fraction in and outside of clouds.

References:

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