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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.

Anonymous Referee #1

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Review of ACP Manuscript # 2003-047, Seifert et al., 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

Overview: The authors of this manuscript use data from instruments aboard the Falcon aircraft during the INCA field campaign to describe thermal properties of both aerosols that formed cirrus crystals (residuals) and particles that did not nucleate ice (interstitials). This is a timely topic in that IPCC 2001 has noted cirrus clouds are of extreme importance in climate change, with the interaction of aerosols and ice formation of particular interest. This paper is well written. The Instrumentation section is clear and

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the volatility technique is an important addition to the suite available to atmospheric researchers. The text contains minimal typos and grammatical errors. 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. Furthermore, the authors do not display a comprehensive knowledge of the literature which would have elucidated the problems with their data and their conclusions. They are forced to speculate, incorrectly, to explain the data. These points are addressed below. I am left to conclude that a rewrite of this manuscript would be too extensive to retain the overall form of the text and reluctantly recommend rejection of this work.

Specific Comments:

1. The cornerstone of this paper is the measurement of ice residuals, that is the particles on which cirrus ice formed and from which condensed phase water was removed. A Counterflow Virtual Impactor, a well know instrument, was used to separate cirrus crystals from the unactivated, or interstitial, aerosol. Ice crystals were heated to cabin temperature ('unheated', 25-30°C) and residuals were then subject to variable heating to determine their thermal stability: non-volatiles (the particles did not evaporate at 250° C), semi-volatile (125° to 250°C), and volatile (particles lost at 125° C). The authors show that as ice crystal concentration increased so did the non-volatile fraction until it dominated the residuals at the highest ice concentrations (up to 10000 per liter after having been converted to ambient concentrations!, pg. 3663 and Figure 3). Likely materials would be mineral dust, soot, or sea salt (pg. 3665) or fly ash or anthropogenic metals (these types should be added). This behavior extended from warm to the cold cirrus sampled ($<$235 K) and was reflected in the interstitial aerosol as well. The authors note that this behavior is 'Ĕopposite of what was expectedĔ' (pg. 3671) and this is, indeed, the case. In fact, this result is non-physical and the arguments made to support it in the Discussion section are incorrect. Specifically, those referenced in the paper (Heymsfield, DeMott, and Karcher) have shown that homogeneous

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freezing by volatile or semi-volatile aerosols should dominate freezing at the lower temperatures and the authors reiterate their points on pg. 3671. 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. A. If I read Figures 1 and 3 correctly, the authors indicate that at ice crystal concentrations up to 10000 per liter 50% of the residuals are non-volatile. The authors suggest that crustal, metallic, or carbonaceous material may be responsible (pg. 3671). The volume concentration of ice nuclei in layers produced by dust storms may contain up to 3000 per liter (DeMott et al., GRL, 2003) but the number found by the authors can be greater than 2 times this amount. A similar amount of non-volatile material was observed in the interstitial aerosol. To my knowledge no dust events occurred during INCA. Soot has never been found in the upper troposphere within orders of magnitude of these quantities (see the Murphy et al. 1998 reference as well as various studies by J.C. Wilson, P. Sheridan, etc.) especially in the southern hemisphere where upper tropospheric air traffic is minimal - where the authors find the largest non-volatile fraction. B. The authors suggest that sea salt may also be responsible for these particles (pg. 3672). According to various references from INDOEX and ACE there may exist 10 sea salt particles per cc less than 100 nm diameter in the marine boundary layer. If such a parcel is lifted to 100 mb - assuming absolutely no losses such as cloud processing - this leaves ˜1 particle per cc. The authors argument would require up to an order of magnitude more, must assume no losses by mechanisms such as precipitation, and is inconsistent with any previous observations in the upper troposphere (see Murphy, Wilson, and/or Sheridan). C. In the fifth paragraph of the Discussion the authors speculate that aerosols in the southern hemisphere are due to long range transport whereas those in the northern hemisphere are locally produced. The scientific consensus is that the lower observed particle concentrations in the southern vs. the northern hemispheres (reference to Minikin et al. 2003 in this paper) are the result of a lower source strength of particles in the southern hemisphere.

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To my knowledge there is no evidence to suggest that particles in either hemisphere has a longer lifetime as suggested by the authors. This could be a local or seasonal phenomena (please see point 3, below) but this speculation is completely unfounded and should be either supported or removed from the manuscript. D. The only possible explanation that I can think of for this data is briefly speculated on in the fifth paragraph of the Discussion: that there are extremely small non-volatile cores (must be $<$20 nm diameter) that no other researcher has observed (i.e., smaller than the size range of Sheridan, Murphy, etc.) within much larger aqueous droplets. Freezing would therefore have been homogeneous, from a particle with a dominant semi-volatile or volatile character. These particles would have, for an unknown reason, been correlated to the most dense cirrus and at the lowest observed temperatures. I can not reason why this would be the case. If this happened then this paper remains incorrect in that the classification categories would be related to a small inclusion in the particles that had a) no effect on the freezing mechanism b) did not describe the chemical or physical nature of the original particle. I am left to conclude that the most likely reason for the authors' 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.

2. The authors describe the thermal stability process: 'unheated': cabin temperature 25-30° C; 'volatile': 125° C; 'semi-volatile': 125-250°C; 'non-volatile': $>$250°C. Cirrus ice, in the cold case, was 235 K (-38°C). By the time the 'unheated' measurements are made the residuals and interstitial have been heated at least 63°, 50% of the 'semi-volatile' temperature range. Urs Baltensperger's group has shown significant modification of aerosols when heated over this temperature range. I would suggest the term 'unheated' is not appropriate and some discussion of the changes induced should be made.

3. The terms Northern Hemisphere (NH) and Southern Hemisphere (SH) are used

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through the Abstract and Introduction. At the beginning of the Experimental section the mission locations, Punta Arenas, Chile and Prestwick, Scotland, are specified. At this point the authors return to the use of NH and SH with blanket descriptions such as pristine, polluted, and clean. I would suggest that NH and SH be replaced by the mission locations. This paper is otherwise misleading in that the reader is drawn to the conclusion that the results are indicative of the entire northern or southern hemisphere whereas measurements were actually only made in two places at one season of the year. Events such as dust storms, biomass burning, and pollution events are hemispheric and seasonal in nature and have an as yet unresolved effect on aerosol number density, lifetime, ice nucleation ability, and cloud formation. I am aware that the use of NH and SH has been used in most INCA publications and the authors are following that lead. The abbreviations are, however, incorrect and prone to misinterpretation and should be removed.

4. The first paragraph of the Introduction describes the formation of ice in the atmosphere, specifically the heterogeneous and homogeneous freezing mechanisms. This topic has been the focus of considerable time by many researchers and yet no references are made here. The authors later reference Karcher, Heymsfield and DeMott. Any of these would be appropriate here, as well as DeMott et al., The susceptibility of ice formation in upper tropospheric clouds to insoluble aerosol components, JGR, 1997. I note that these works underline the non-physical nature of the arguments made in this paper.

5. The second paragraph of the Introduction describes the previous work by the author showing 'Ĕ cirrus crystals Ĕ controlled by particles smaller than 0.1 mm diameter.' The authors later reference Chen et al., 1998 which shows a larger heterogeneous mode size with few particles at or smaller than 0.1 mm nucleating ice. These results are inconsistent, yet Chen is used to support the assertion that metallic, crustal, or soot particles are responsible for the observations described in this work. As with the previous point the relation of this work to the relevant literature is lacking.

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6. I note that the authors simultaneously published a companion paper in ACP. There is a lead-in to this paper on pg. 3666 (Results, second paragraph) as the authors speculate the connection of their data to the lifecycle of a cirrus cloud. I have three serious reservations about this paragraph and the companion paper:

A. The upper third of Figures 1 and 3 are extremely suspect, the remainder at least questionable. This is extended to Figures 3, 5 and 10 of the companion paper. Can the conclusions drawn in the companion paper be justified in this light? B. The authors discuss the cirrus lifecycle in this paragraph as a combination of RH and Ncvi. No mention is made of the effect of aircraft sampling on this diagram. Specifically, not all clouds have the same maximum crystal density due to formation mechanism (i.e., presence of efficient ice nuclei, water vapor, uplift velocity). Therefore, a cloud with many IN may appear in the lower left, not the lower right, part of the diagram (i.e., cloud growth occurring in a space defined as evaporation). Likewise, a subvisible cloud might 'live' only in the lower right portion of the figure (evaporating in the space in which other clouds grow). The observer (i.e., the aircraft instrument) has no means to know the parcel history and, therefore, can not accurately understand what portion of the diagram a mature cloud occupies (see also Figure 3 in the companion paper). How will this effect the conclusions? C. Data is presented to 20% RH. Can data at less than about 60%, 80% be considered part of a cloud?

Technical Comments: The text is well written with minor errors. 1. Please correct line 21, page 3668: 'Ěto an aboutĚ' 2. Two temperature scales should not be used; please use either K or °C. 3. The color scales in Figures 1 and 2 should be consistent; ' hot colors' should represent the same fraction throughout.

Interactive comment on Atmos. Chem. Phys. Discuss., 3, 3659, 2003.

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