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analysis of particles

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# 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

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## Abstract

A thermal volatility technique is used to provide indirect information about the chemical composition of the aerosol involved in cirrus cloud formation. The fraction of particles that disappears after being heated to 125°C is termed volatile and the fraction that disappears between 125 and 250°C is termed semi-volatile. Particles that still remain after being heated to 250°C make up the non-volatile fraction. The thermal composition of residual particles remaining from evaporated cirrus crystals is presented and compared to interstitial aerosol particles (non-activated particles in between the cirrus crystals) for two temperature regimes (cold:  $T < 235\text{K}$ , warm:  $235 \leq T < 250\text{K}$ ), based on in-situ observations. The observations were conducted in cirrus clouds in the Southern Hemisphere (SH) and Northern Hemisphere (NH) midlatitudes during the INCA project. In the cold temperature regime, the non-volatile fraction of the residual particles was typically in the range 10 to 30% in the NH and 30 to 40% in the SH. In the warm temperature regime, the non-volatile residual fraction was typically 10 to 30% (NH) and 20 to 40% (SH). At high crystal number densities the non-volatile fraction in both temperature regimes was even higher: in the range of 30 to 40% (NH) and 40 to 50% (SH). The semi-volatile fraction was typically less than 10% in both hemispheres, causing the volatile fraction to essentially be a complement to the non-volatile fraction. In terms of the fractioning into the three types of particles, the SH cold case is clearly different compared to the other three cases (the two warm cases and the cold NH case), which share many features. In the NH data the distribution of different particle types does not seem to be temperature dependent. In all the cases, the non-volatile fraction is enriched in the residual particles compared to the fractions observed for the interstitial particles. This enrichment corresponds to about 15 (NH) and 30 (SH) percent units in the two cold cases and to 15–25 (NH) and 25–35 (SH) percent units in the two warm cases. In the NH cold case, there is a clear relation between the fractions observed in the interstitial particles and what is observed in the residual particles. The observed large fractions of non-volatile particles show that particles forming ice crystals are not

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entirely made up of water-soluble sulfate particles.

## 1. Introduction

Indirect climate forcing can be viewed as a series of microphysical processes that connect anthropogenic emissions to changes in cloud albedo and cloud occurrence. A more detailed understanding of the properties of the cloud forming particles such as Cloud Condensation Nuclei (CCN) and Ice Nuclei (IN) is important for assessing natural and anthropogenic impacts by aerosols on clouds and climate. While the aerosol induced change in cloud droplet spectrum in low clouds has been studied extensively and the formation of warm clouds is relatively well understood, the formation of ice crystals is rather complex and the role of the aerosol remains uncertain. This is mainly due to the fact that ice crystals may form through two different processes: homogeneous and heterogeneous nucleation. The relative role of different modes of ice nucleation is still a matter of debate but is thought to critically depend on temperature. Presumably homogeneous nucleation (freezing of a solution droplet) dominates at low temperatures ( $T < 235$  K), but heterogeneous nucleation (an IN initiates freezing) can become important at higher temperatures, in weaker updrafts or in the presence of large numbers of IN.

The more details we learn about the nature of the aerosols that form cirrus clouds the more intriguing the mechanisms appear. Seifert et al. (2002) showed that the number density of particles contained in cirrus crystals was controlled by particles smaller than  $0.1 \mu\text{m}$  in diameter. On the other hand, the volume density was dominated by particles larger than  $0.1 \mu\text{m}$ . These particular features presented only small differences between observations performed in the pristine Southern Hemisphere (SH) midlatitudes and observations performed in the more polluted Northern Hemisphere (NH) midlatitudes. Seifert et al. (2003) showed that the crystal number density did not increase monotonically with increasing aerosol number density, and that there is a mean crystal number density maximum around  $2 \text{cm}^{-3}$  in the aerosol range  $100$  to  $200 \text{cm}^{-3}$ . Also,

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with respect to these findings, the pristine and more polluted environments presented more similarities than differences. In contrast to the small differences between SH and NH mentioned above, Ström et al. (2003) and Haag et al. (2003) concluded that the cirrus formation threshold with respect to relative humidity over ice was in the range of 20 to 25% units lower in the NH midlatitudes compared to the SH. The formation threshold for the SH was consistent with homogeneous nucleation.

The chemical composition of the ice forming particles is one of the least understood aspects of cirrus clouds. Recently, Murphy et al. (1998) have shown the composition of upper tropospheric aerosol to be very diverse, challenging the traditional view that aerosol composition in the upper troposphere is dominated by sulfates. The chemistry of aerosol particles incorporated in ice crystals during cloud formation might therefore be more complex than previously treated by most numerical simulations. Heintzenberg et al. (1996) and Twohy and Gandrud (1998) using single particle analysis, showed that minerals dominated the composition of particles larger than a few hundred nanometers in diameter. However, compared to the total population of ice forming particles, these rather large particles are very few.

To explore the chemical composition of smaller particles, we deployed for the first time the thermal volatility technique coupled to a CVI (Counterflow Virtual Impactor). This technique provides no direct information about the chemical composition, but offers a method to investigate the thermal stability of particles in the size range that controls the crystal number density. We contrast observations made in the pristine environment of the SH to observations performed in the more polluted NH midlatitudes.

## 2. Experimental

The INCA (Interhemispheric differences in cirrus properties from anthropogenic emissions) project included two field campaigns in Punta Arenas, Chile (54° S) and Prestwick, Scotland (53° N). The Punta Arenas campaign (10 flights) was performed in March/April 2000 and the second campaign (9 flights) from Prestwick was conducted

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in September/October 2000. This made the seasons equivalent. The aircraft Falcon, operated by Deutsches Zentrum für Luft- und Raumfahrt, was extensively equipped with instrumentation to measure aerosol and cloud microphysics. In addition, a trace gas payload was also deployed to characterize air masses. Tracers used in this study were limited to water vapor, CO and O<sub>3</sub>. The instruments have already been described, however a short description is provided below.

## 2.1. Instrumentation

### 2.1.1. Sampling inlets and cloud probes

Cirrus crystals were sampled using a Counterflow Virtual Impactor (CVI) inlet. The CVI is a device which inertially separates cloud elements larger than about 5 μm and smaller than about 60 μm (aerodynamic size) in diameter from the surrounding atmospheric air (Ogren et al., 1985; Noone et al., 1988). Residual particles left behind by the evaporating cloud elements are analyzed downstream the inlet. Each crystal is assumed to leave only one residual particle behind, which has proven to be a valid assumption (Seifert et al., 2002). The design of the CVI probe causes an enrichment of the crystal number density in the sample air compared to ambient conditions. The enrichment factor was typically around 150. Hence, residual number densities are originally enhanced, but all data presented in this study has been corrected back to ambient conditions.

Aerosol particles were sampled with a ¼ inch stainless steel tube with the opening turned opposite to the flight direction. Due to inertia, large particles pass by the probe and only small particles (D<sub>p</sub> < 1 μm) enter the sample flow (Schröder and Ström, 1997).

The Polar Nephelometer probe is designed to measure the optical parameters of clouds containing either water droplets or ice crystals, or a mixture of these particles. The sensor measures the scattering phase function of an ensemble of cloud particles intersecting a collimated laser beam (Gayet et al., 1997). With the direct measurement of the scattering phase function cloud optical parameters can be calculated, making it

possible to distinguish between water droplets and ice particles.

### 2.1.2. Residual and interstitial aerosol properties

Inside the aircraft, sample air is fed into three separate branches for thermal discrimination. The first branch is unheated and the sampling line is at cabin temperature, which is approximately 25 to 30°C. The other two branches are heated to 125 and 250°C, respectively. Following this, the number density of the remaining particles in each branch is determined by CPCs and referred to as  $N_{30}$  ( $T \approx 25\text{--}30^\circ\text{C}$ ),  $N_{125}$  ( $T = 125^\circ\text{C}$ ) and  $N_{250}$  ( $T = 250^\circ\text{C}$ ).

Two of these thermal denuder systems were used, one for the residual particles from the CVI probe, and the other for the interstitial and out-of-cloud aerosol. The interstitial aerosol lines were connected to four CPCs (model TSI 3010). The particle counters connected to the non-volatile and semi-volatile branches had a cut-off at 10 nm. The two particle counters connected to the interstitial non-heated branch had cut-offs at 5 and 14 nm, respectively. To overcome this problem of different cut-offs, an average between these two CPCs was used to emulate a counter with a cut-off comparable to the two other heated branches. The approximated number density of interstitial aerosol particles larger than 10 nm in the non-heated branch will be referred to as the interstitial aerosol number density ( $N_{int}$ ). For the residuals the non-heated CVI sampling line was connected to a CPC model TSI 3010 with cut-off at 10 nm. The total residual number density (non-heated sample line) is referred to as  $N_{cvi}$ . The two heated sample lines were connected to modified CPCs (model TSI 3760) using forced cooling (Schröder and Ström, 1997). Post campaign laboratory calibration showed that the TSI 3010 and the two modified TSI 3760 had the same 50% efficiency cut-offs, but the slope of the efficiency curve was flatter for the two modified counters.

The thermal denuder technique provides indirect information about the chemical composition of the aerosol (Clarke, 1991). If particles disappear at 125°C the composition is consistent with sulfuric acid and some organic species. If the particles disappear at 250°C the composition is consistent with ammonium sulfate or ammonium bi-sulfate.

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If particles still remain after heating to 250°C the composition is consistent with e.g. minerals, soot, or sea salt. Note that we do not know what the particles are made of, only that their thermal stability is consistent with the various types of compounds mentioned. By comparing the different number densities ( $D_p > 10$  nm), we can derive three fractions  $(N_{30} - N_{125})/N_{30}$ ,  $(N_{125} - N_{250})/N_{30}$  and  $N_{250}/N_{30}$ , which are referred to as the volatile, semi-volatile and non-volatile fractions.

### 2.1.3. Trace gases

Relative humidity was measured by a cryogenic frost point hygrometer (Ovarlez et al., 2000). From the primary measurement of the frost point we derived the relative humidity over ice, which will be referred to as RH<sub>i</sub>. In addition we made use of CO to identify recent transport of polluted air from the boundary layer and O<sub>3</sub> to identify the likely influence of stratospheric air. The instruments used have already been described (Gerbig et al., 1996; Schlager et al., 1997).

Data is stored at 1 Hz. In order to smooth the data we applied a 6 s moving average to the data while still preserving much of the temporal resolution.

### 2.2. Data selection

The data sets used in this study were selected to represent cirrus observations in the upper troposphere and tropopause region. Stratospheric observations were excluded based on ozone profiles, and only measurements made above 6 km altitude and below 250 K temperature were used. A minimum crystal number density of  $0.001 \text{ cm}^{-3}$  was used to separate between cloudy and non-cloudy data points. In-cloud data points with the presence of liquid water, observed down to 239 K, were excluded based on the Polar Nephelometer measurements. Finally, the influence by polluted air masses recently transported from the boundary layer (i.e. via convective clouds) was reduced by excluding data points where the CO mixing ratios exceeded 90 ppbv. The remaining data, 21 h from the SH and 12 h from the NH, was divided into two temperature regimes



(cold:  $T < 235$  K and warm:  $235 \leq T < 250$  K). This temperature division is based on the notion that the mode of freezing at temperatures below ca. 235 K is expected to be dominated by homogeneous nucleation. Note that warm temperature data makes up for less than 20% of the total observation time in both hemispheres.

### 3. Results

#### 3.1. Thermal composition of residual particles

Figure 1 shows the average fraction of volatile, semi-volatile and non-volatile residual particles as a function of  $N_{cvi}$  and  $RH_i$ , separated into campaign and temperature intervals. The figure is organized in panels as follows: particle types in columns and temperature intervals and campaigns in rows. The first row (panels a–c) represents the NH cold temperature regime data, the second row (panels d–f) represents the NH warm temperature regime data, the third row (panels g–i) represents the SH cold temperature regime data and finally, the fourth row (panels j–l) represents the NH warm temperature data.

Assuming that cirrus clouds form at high relative humidities and dissipate at low relative humidities, we can view different combinations of  $N_{cvi}$  and  $RH_i$  in the following way: Prior to cloud formation the relative humidity is above 100% and no cirrus crystals exist. Once a cloud forms, data will show up in the bottom right part of a panel. In the early phase of the cloud lifecycle the crystal number density increases rapidly without changing the ambient humidity very much. When enough ice mass has been formed, ice growth depletes available water vapor faster than it is supplied. At that time, the ambient relative humidity and the crystal number density will be at their maximum. From then on the existing crystals continue to grow in size until the humidity has relaxed to 100%. As the relative humidity decreases further the crystals begin to evaporate causing the cloud elements to disappear. Based on the combination of  $RH_i$  and  $N_{cvi}$  we can get a sense of what phase of the lifecycle the cloud is. In other words, whether

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the cloud is in the forming, maturing, or its dissipating phase. This way of plotting cirrus related data has previously been used by Ström et al. (2002) and Seifert et al. (2003).

If neighboring combinations of RH<sub>i</sub> and N<sub>cv</sub>i were uncorrelated, we would expect to observe a mosaic pattern without any coherent structures. Clearly the color patterns in most panels of Fig. 1 display regions with similar color coding. Note that there are many cells lacking data in the warm temperature panels, which is due to the fact that less than 20% of all our cirrus observations were made above 235 K.

The color coding of the volatile particles (left column of panels) shows fractions typically above 50%. The gradient from warm to cold colors indicates that the volatile fraction decreases mainly with increasing N<sub>cv</sub>i but also slightly with increasing RH<sub>i</sub>. The two NH panels and the warm SH panel are very similar in appearance whereas the cold SH panel stands out in comparison. The colors in the cold SH panel are not as warm as in the other three panels and there are gradients in the color coding towards both higher and lower N<sub>cv</sub>i.

The color coding of the semi-volatile particles (center column of panels) shows fractions typically less than 10%. In contrast to the volatile fractions there are no clear gradients in color coding apparent for the NH cold case and both SH cases. For the NH warm case there is a suggestion of relatively higher fractions at high N<sub>cv</sub>i and high RH<sub>i</sub> coordinates.

Due to the relatively small semi-volatile fractions, the non-volatile fraction (right column of panels) is essentially a complement to the volatile fraction. The similarity between the two NH panels and the warm SH panel is perhaps more obvious in the case of the non-volatile fraction. The difference between high and low relative humidity is pronounced in the two cold cases. As the humidity increases, the fraction of non-volatile particles increases.

The data in the first and third row of Fig. 1 consists only of data sampled at temperatures below 235 K. According to theory this temperature range should be dominated by homogeneous freezing of solution droplets formed on soluble cloud condensation nuclei (CCN). It is therefore somewhat unexpected to find that typically 10 to 30 % (NH)

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and 30 to 40% (SH) of the residual particles are of non-volatile nature and at high Ncvi the non-volatile residual fraction corresponds to as much as 30 to 40% (NH) and 40 to 50% (SH). In the warmer temperature interval the fraction of non-volatile residuals was typically between 10 to 30% (NH) and 20 to 40% (SH). We note that the cold NH case shares more features with the two warm cases than with the cold SH case.

The fraction of ambient aerosol particles incorporated in the ice crystals is small and typically less than 1% (Seifert et al., 2002). Therefore, nucleation scavenging is not expected to significantly affect the ambient aerosol. Treating the ambient aerosol in the same fashion as the crystal residues provides us with a possibility to compare the phase partitioning of volatile, semi-volatile and non-volatile particles. In the next section we proceed by presenting the ambient aerosol analogously to the crystal residues in Fig. 1.

### 3.2. Thermal composition of interstitial aerosol particles

In Fig. 2 the volatile, semi-volatile and non-volatile fractions for the non-activated interstitial aerosol are shown, divided into campaign and temperature interval. As pointed out for the residual particle data presented above, if neighboring cells or combinations of RHi and Ncvi were not related we would expect to observe a pattern without any coherent structures.

Volatile particles (left column of panels) typically correspond to more than 50% of the particles in the NH. The volatile fractions in the SH display warmer colors corresponding to an about 10 and 20% units higher fraction for the cold and warm case, respectively. Of the four panels to the left, the SH warm case stands out a little with generally warmer colors throughout the domain. Semi-volatile particles (center column of panels) were below 30% in the two NH cases and the SH cold case, whereas in the SH warm case this fraction was typically below 20%. The non-volatile fraction (right column of panels) was typically below 15% in both hemispheres, with the exception of the SH warm case where the non-volatile fraction was less than 5%.

The panels presented in Fig. 2 lack distinct gradients in color coding as can be seen

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in most panels of Fig. 1. However, some noticeable features are evident in particular for the cold cases. In the NH data high  $N_{cvi}$  is associated with a relatively high fraction of non-volatile particles. The semi-volatile fraction in the SH cold case, on the other hand, is found to be low at high  $N_{cvi}$ , with the opposite holding true for the NH semi-volatile fraction.

We use the data presented in Figs. 1 and 2 to study if there is a relation between the properties of the ambient aerosol and the particles incorporated into cirrus crystals.

### 3.3. Relation between thermal properties of ambient aerosols and residual particles from ice crystals

If one compares the panels of the residual and interstitial particles, it becomes obvious that the relative contributions of the volatile, semi-volatile and non-volatile particles differ significantly. In the cold cases the non-volatile fraction in residual particles is about 15 (NH) and 30 (SH) percent units higher than in the ambient air. In the two warm cases this enrichment corresponds to 15 to 25 and 25 to 35% units for the NH and SH, respectively. The opposite relation is true for the semi-volatile fractions.

To make the relation between crystal residues and ambient aerosol particles clearer we narrow our data set to only include the mature stage of the cloud and exclude the most transient parts of the cloud evolution. To do this we use data where the relative humidity over ice is in the range of 95 and 105%.

The resulting data is then classified according to  $N_{cvi}$  in bins and the average volatile, semi-volatile and non-volatile residual and interstitial fractions are calculated. In Fig. 3 the fractions are plotted as the relative deviation from the mean fraction calculated for the humidity range 95 to 105%.

In the case of the NH cold data, the volatile, semi-volatile and non-volatile fractions of the residual and interstitial particles covariate in their deviations from the mean as a function of  $N_{cvi}$ . The NH warm interstitial aerosol fractions suffer from lack of data, but in the warm temperature regime we find the non-volatile residual fraction to increase with crystal number density, much like in the case of cold data. However, only in the NH

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data the interstitial trends are close to the trends of the residual data. We note that the deviations from the mean are generally smaller in the SH data, which is especially true for the interstitial non-volatile data showing no response to changes in crystal number density.

5 To summarize, in the NH cold case there is a clear relation between the respective fractions of particles in the ambient air and the fractions of the residual particles. The volatile fraction decreases with increasing crystal number density, whereas the semi-volatile and the non-volatile fractions increase with increasing  $N_{cvi}$ .

10 Vertical wind and temperature are important in controlling the crystal number density in cirrus (Kärcher and Ström, 2003). Nevertheless, in the NH the non-volatile particle fraction in crystals and in the ambient air is related to crystal number densities. If the non-volatile fractioning of the crystal residues increases due to an increase in the ambient aerosol non-volatile fraction, or if there is simply a causal relation between crystal number densities and the fractioning of particle types, is not known. However,  
15 the fact remains that the NH data and the SH data show distinctively different behavior when it comes to the fractioning of particle types in ice crystals and interstitial air.

#### 4. Discussion

Our observations clearly show an enhancement of the non-volatile fraction of the residual particles compared to the interstitial aerosol. Typically 10 to 30% (NH) and 30 to  
20 40% (SH) of the residual particles are non-volatile at temperatures below 235 K. The semi-volatile fraction is typically low, essentially making the volatile and the non-volatile fractions into complements. The highest fractions of non-volatile residual particles were found at high crystal number densities and high relative humidities. Of the four cases (NH warm and cold, and SH warm and cold) the SH cold case presented the highest  
25 fractions. The other three cases presented smaller values, but at the same time they also had more points of similarity.

At temperatures below 235 K homogeneous freezing is believed to be the dominant

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mode of ice nucleation. It is therefore somewhat surprising that at high crystal number densities as much as 30 to 40% (NH) and 40 to 50% (SH) of the particles in cirrus crystals remain after heating the sample air to 250°C. Based on homogeneous nucleation theory the water activity of a particle will determine the probability of spontaneous freezing (Koop et al., 2000). Large particles composed of hygroscopic material will thus have a higher probability of freezing than small particles. Aerosol particles acting as CCN in the upper troposphere are believed to mainly consist of varying mixtures of NH<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub> and H<sub>2</sub>O. These are compounds that are not stable at 250C and particles composed of them will evaporate and not be detected by the particle counters.

The data presented by Seifert et al. (2002) shows that there is no strong preference for ice nucleation to occur on large aerosol particles to the extent expected for homogeneous nucleation (e.g. Heymsfield and Sabin, 1989; DeMott et al., 1994; Jensen et al., 1998). The large fraction of non-volatile particles found in ice crystals may be a clue to why this is so. Aerosol particles acting as heterogeneous IN may be crustal, metallic, or carbonaceous material (Chen et al., 1998), in other words, chemical species that are likely to remain after heating to 250°C.

The importance of heterogeneous nucleation compared to the competing homogeneous nucleation depends not only on the number of potent freezing agents, but also on updraft and temperature. Heterogeneous nucleation is believed to become important in weaker updrafts (associated with low N<sub>cv</sub>) and at higher temperatures (e.g. Sassen and Benson, 2000). Based on this we expect a larger non-volatile fraction of residual particles at low N<sub>cv</sub>, as well as low non-volatile fractions at cold temperatures. In Fig. 1 we see that low N<sub>cv</sub> is actually associated with relatively low non-volatile ratios in all cases but the SH warm case. The NH warm and cold cases and the SH warm case present similar fractions. The SH cold case, however, actually shows much higher non-volatile fractions than the SH warm case. In other words, more or less the opposite of what was expected is observed if non-volatile particles are associated with heterogeneous IN.

Even if a particle is classified as non-volatile the nucleation mechanism may still

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be homogeneous if the particle is a mixture of different compounds (volatile and non-volatile). Volatility analysis is based on the fact that many aerosol species dissociate and evaporate at characteristic temperatures. As an aerosol is heated particles lose mass as their chemical constituents volatilize resulting in changes in the size distribution. For an externally mixed aerosol the change in size distribution is characterized by the removal of particles arising from the same source. For an internally mixed aerosol the interpretation of the volatility data is not straightforward. Increasing the temperature causes volatile species to disappear, but may also cause the physical separation of particle constituents. Hence thermal treatment may (1) shift the size spectrum to smaller diameters but the number density stays constant, (2) shift the size spectrum to smaller diameters but the number density increases or (3) shift the size spectrum to smaller sizes and the number density decreases. The complex thermal behavior of an internally mixed aerosol has been recently investigated by Brooks et al. (2002).

But why is the non-volatile fraction so pronounced in the SH cold case? Recently, Minikin et al. (2003) has shown for the INCA data that the aerosol number density in the NH is more variable and typically a factor of 2–3 higher than in the SH. This would point towards a more aged aerosol in the SH where transformation processes during long-range transport become increasingly important to characterize the aerosol the further away from sources the air mass gets. In the SH the aerosol properties are more characterized by long-range transport compared to the NH where sources at the surface may play a larger role. Hence a particle not necessarily suitable for forming an ice crystal may acquire a significant coating of soluble material by condensation and coagulation that transforms the particle to a potential ice-forming particle. When humidity increases the particle may turn into a solution droplet with an insoluble core. The other possibility is that non-volatile particles are NaCl particles. These are very hygroscopic, but would not volatilize at 250C. The SH midlatitudes are mainly ocean and a large source of sea-salt particles. We know that most of the particles forming ice crystals are smaller than 0.1  $\mu\text{m}$  in diameter (Seifert et al., 2002), which would have to hold for the sea-salt particles as well. In laboratory studies Mårtensson et al. (2003)

have shown that many small NaCl particles indeed do form during bubble bursting.

It is possible that the non-volatile residual particles in the SH are chemically different from the non-volatile residual particles in the NH. Direct measurements of the chemistry of the residual particles are required to learn what these non-volatile particles are composed of.

## 5. Summary and conclusions

The goal of this study was to investigate the phase partitioning of aerosol particles in cirrus clouds with respect to thermal composition to obtain some indirect information about whether the chemical characteristics of aerosol particles play a role in ice nucleation. The major conclusions of this study are as follows:

1. In the cold temperature regime the non-volatile residual fraction typically corresponds to 10 to 30% (NH) and 30 to 40% (SH). In the warm temperature regime the non-volatile residual fraction was typically 10 to 30% (NH) and 20 to 40% (SH). At high crystal number densities the non-volatile fraction was even higher and in the range of 30 to 40% (NH) and 40 to 50% (SH) for both temperature regimes.
2. The semi-volatile residual fraction was typically small, less than 10%, essentially causing the volatile and the non-volatile fractions to be complements.
3. Compared to the ambient aerosol particles, the fraction of non-volatile particles is enriched in the crystal residuals by 15 (NH) and 30 (SH) percent units in the cold cases. For the two warm cases this enrichment corresponds to 15 to 25 (NH) and 25 to 35 (SH) percent units.
4. In the NH cold case there is a clear relation between the fraction of non-volatile particles in the ambient air and the non-volatile fraction of the residual particles. Both increase with increasing crystal number density.

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5. The NH cold case has more in common with the NH and SH warm cases than with the SH cold case. Hence the chemical signature of the residual particles in the NH appears to be temperature independent.

By coupling a thermal denuder system to a CVI probe we have for the first time been able to get some insight into the chemical nature of the numerous small ice crystal residuals. The perhaps unexpectedly large fraction of non-volatile particles, especially at cold temperatures, and the lack of temperature dependence in the NH data, suggests that cirrus formation might not simply be divided into homogenous or heterogeneous modes depending on temperature.

The simple thermal denuder system used in this study is limited by only treating integral number densities. A system that would provide size resolved information would really help in understanding the link between aerosols and cirrus formation. A volatility tandem DMA technique would not only provide size resolved information, but would also give a direct measurement of the internal and external mixture of the aerosol.

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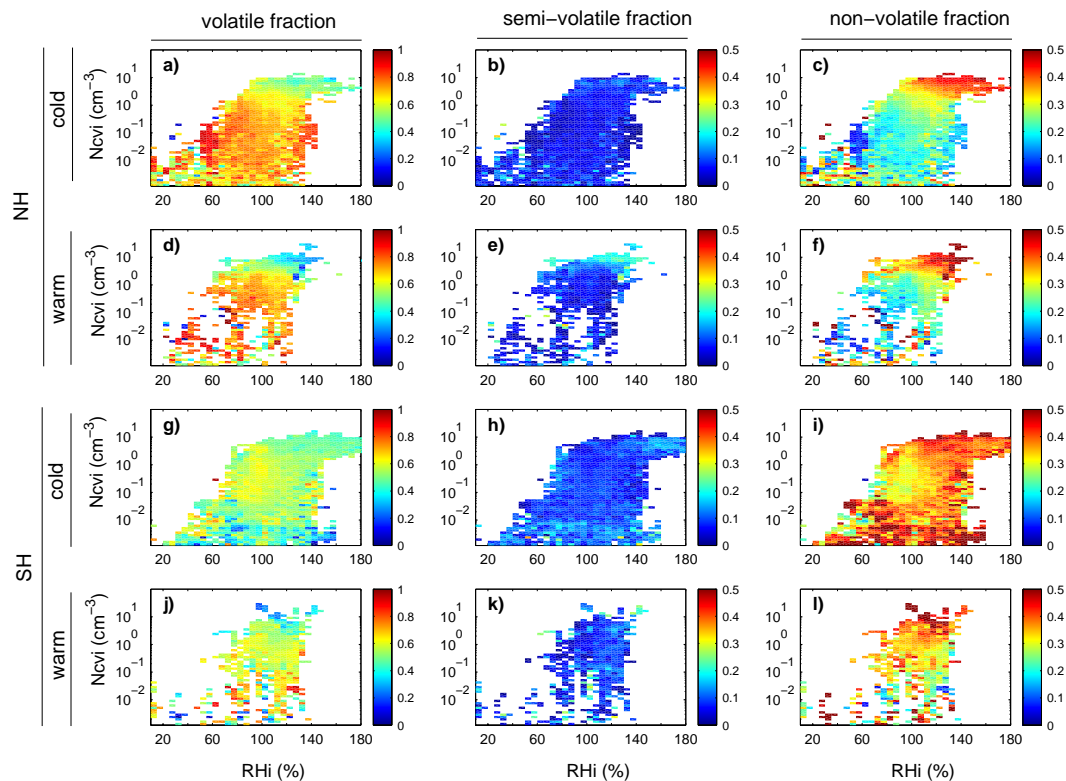
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**Fig. 1.** Average volatile (left column), semi-volatile (middle column) and non-volatile (right column) residual particle fraction as a function of RH<sub>i</sub> and Ncvi. Data divided into campaign (NH,SH) and temperature interval (cold:  $T < 235$  K, warm:  $235 \leq T < 250$  K). NH-cold (**a–c**), NH-warm (**d–f**), SH-cold (**g–i**), SH-warm (**j–l**). Note the different color scales.

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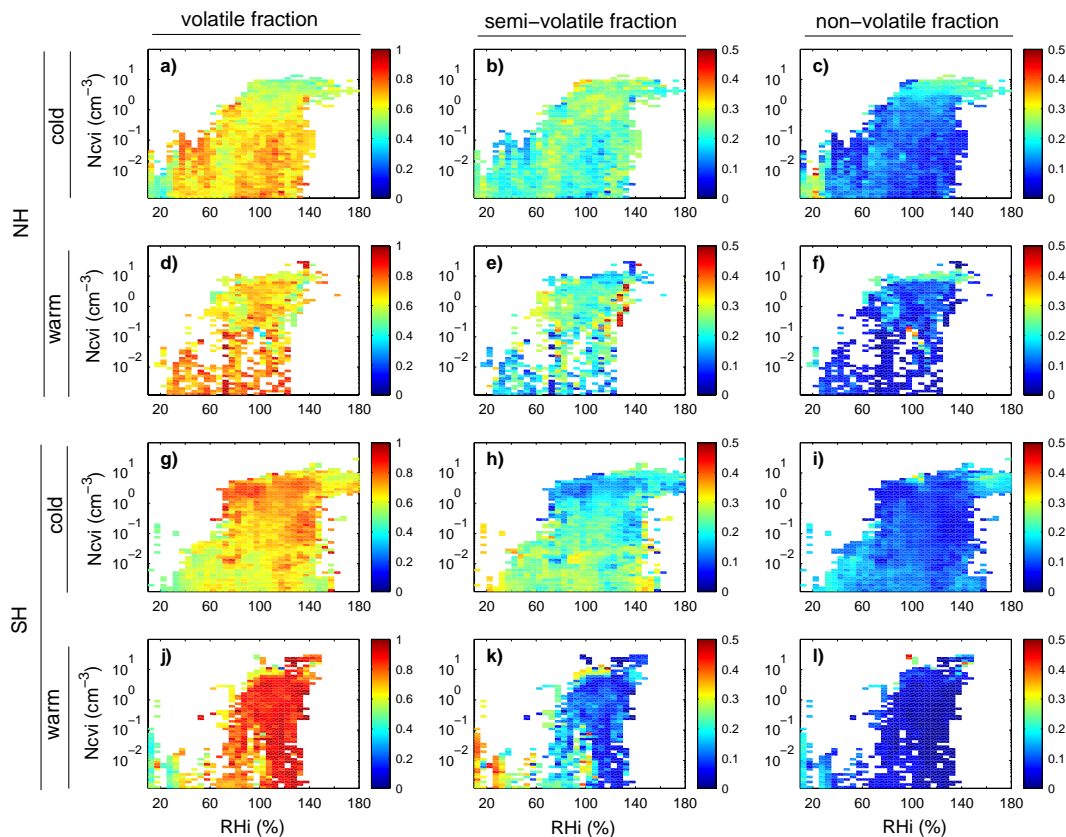
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**Fig. 2.** Average volatile (left column), semi-volatile (middle column) and non-volatile (right column) interstitial aerosol fraction as a function of RHi and  $N_{cvi}$ . Data divided into campaign (NH, SH) and temperature interval (cold:  $T < 235$  K, warm:  $235 \leq T < 250$  K). NH-cold (**a–c**), NH-warm (**d–f**), SH-cold (**g–i**), SH-warm (**j–l**). Note the different color scales.

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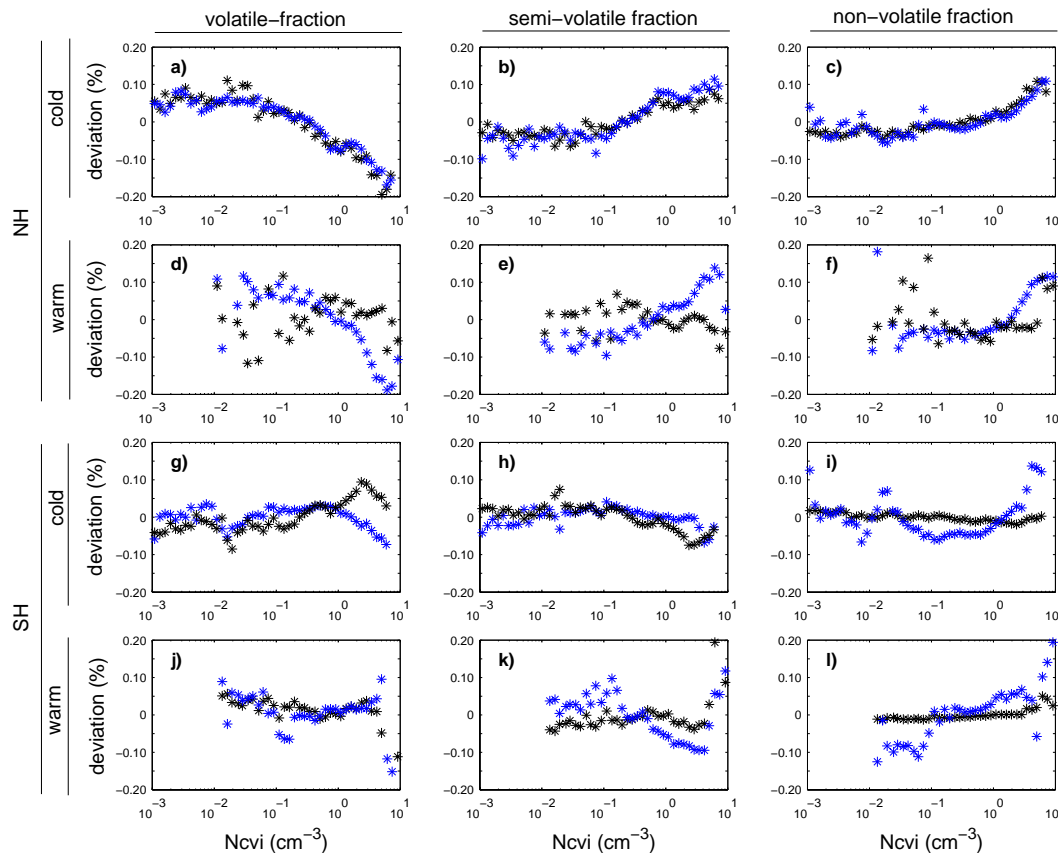
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**Fig. 3.** Deviation from the average volatile (left column), semi-volatile (middle column) and non-volatile (right column) particle fraction as a function of  $N_{cvi}$  shown as blue stars for the residuals and black stars for the interstitial aerosol. Data divided into campaign (NH, SH) and temperature interval (cold:  $T < 235$  K, warm:  $235 \leq T < 250$  K). NH-cold (a–c), NH-warm (d–f), SH-cold (g–i), SH-warm (j–l).

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