# PHYSICO-CHEMICAL CHARACTERISATION OF ICE PARTICLE RESIDUALS IN TROPOSPHERIC MIXED-PHASE CLOUDS BASED ON ICE PARTICLE COLLECTION USING THE COUNTERFLOW VIRTUAL IMPACTOR TECHNIQUE

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## 1. INTRODUCTION

The nucleation of ice particles in middle and lower tropospheric clouds can initiate precipitation and change cloud optical properties, thus affecting the radiative forcing of supercooled clouds [Lohmann and Feichter, 2005]. In mixed-phase clouds of the lower and middle troposphere heterogeneous nucleation, which is triggered by a subset of atmospheric particles named ice nuclei (IN), is the dominant process initiating primary ice formationat temeratures above -38 °C. The heterogeneous ice formation can proceed via different mechanisms [Cantrell and Heymsfield, 2005] which include the creation of new frozen hydrometeors by deposition and condensation freezing or icing of existing cloud drops via contact, immersion or evaporation freezing.

Closely related to the heterogeneous ice nucleation process is the question of the physico-chemical IN properties. Our knowledge about atmospheric particles that act as ice nuclei in tropospheric mixed-phase clouds is incomplete, because the ice phase develops in between super-cooled drops, which complicates the experimental and theoretical investigation.

For this reason a ground-based sampling device was developed in order to extract small ice particles from tropospheric mixed-phase clouds and to identify the size and chemical composition of their residues by state-of-the-art analysis methods [Mertes et al., 2007]. These measurements have been carried out within the cloud and aerosol characterization experiments (CLACE) at the high alpine research station Jungfraujoch (Swiss Alps, 3580 m asl).

## 2. EXPERIMENTAL

This sampling system is based on a counterflow virtual impactor (CVI), which cannot distinguish between frozen and liquid hydrometeors of the same aerodynamic size. Large particles are additionally sampled, so that in mixed-phase clouds the residues include cloud condensation nuclei (CCN) and scavenged interstitial particles besides the desired IN. Thus, the novel inlet, called Ice-CVI, is supplemented with further components to avoid the collection of supercooled drops and large ice particles. A vertically oriented inlet horn in combination with a virtual impactor (VI) removes the precipitating ice particles larger than 20 µm. The upper limit of 20 µm assures an aspiration efficiency of nearly one for the sampled small ice particles. Downstream of the VI a pre-impactor (PI) segregates the super-cooled drops by their freezing at

contact on cold impaction plates. The remaining ice particles bounce off without significant shattering due to their small size and low velocity and remain in the sample airflow. The CVI itself is located downstream of the PI to reject interstitial particles smaller than 5 µm by a controlled counterflow. Inside the CVI the small ice particles are injected into a particle-free and dry carrier air leading to their complete evaporation, and the released dry residual particles are analyzed.

## 3. RESULTS

Results will be presented from CLACE 4, 5 and 6 carried out in February/March 2005, 2006 and 2007, respectively.
Background aerosol particles were sampled before, during and after a cloud event by means of a total aerosol inlet and analyzed in the same way as the ice particle residues in order to identify special features of the IN physico-chemical properties.
Mean background aerosol and ice particle residue number size distributions measured with two scanning mobility particle sizers (SMPS) simultaneously during two different cloud events are shown in Fig.1.

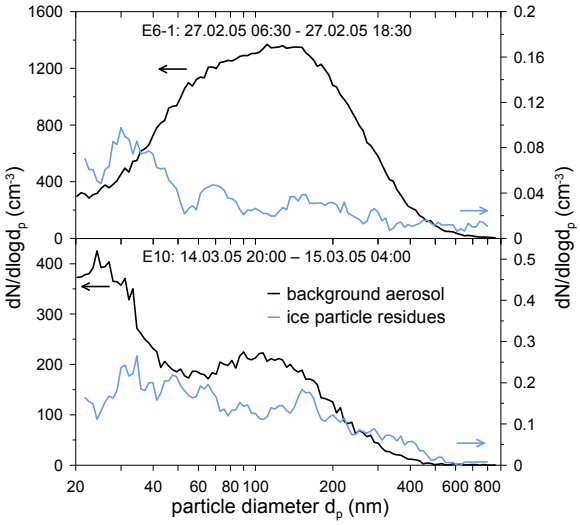


***Fig.1**: Mean background aerosol (black line) and ice particle residue (blue line) number size distributions measured with two scanning mobility particle sizers (SMPS). The latter is linked to the right y-scale.*

Averaging times are several hours due to the very low concentration of the ice particle residues. It is obvious that the background aerosol particle number size distributions have different but distinct modes whereas the residual particle number size distributions show no clear structures. However, a weak minimum around 100 nm is visible with a slight increase of residual particles to smaller sizes. These residues are not considered to have served as ice nuclei but most likely to stem from small secondary ice particles. Those ice particles are expected to be generated by rime splintering, ice-ice collisions and fragmentation during drop freezing in mixed-phase clouds [e.g. McFarquhar et al., 2007]. Part of these secondary ice particles should be smaller than 20 µm [Fridlind et al., 2007] and thus sampled by the Ice-CVI. Since they mainly contain scavenged interstitial particles and/or part of the soluble material of the frozen drop they release rather small residues after their evaporation in the CVI. This consistently explains the occurrence of residual particles below a diameter of about 100 nm. Assuming that only residual particles larger than 100 nm acted as ice nuclei results in IN number concentrations of about 0.17 and 0.08 cm$^{-3}$ for the two cloud events presented in Fig.1.

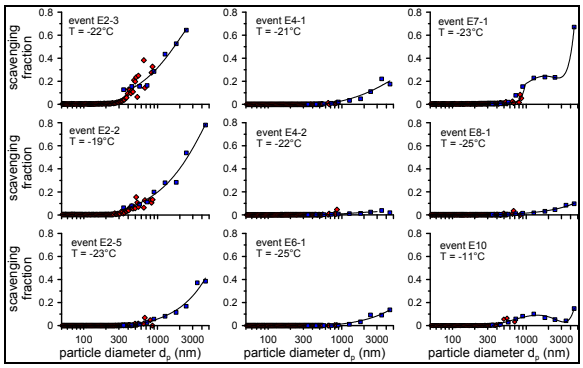


***Fig.2**: Scavenged number fractions of IN as a function of their particle size. Diamonds (red) and squares (blue) present SMPS and OPC measurements, respectively.*

Dividing the ice particle residue distributions by those of the background particles yields

the number fraction of IN as a function of particle size. This scavenging fraction is plotted in Fig.2 extended to the super-micrometer size range using data from two optical particle counters (OPC) operated simultaneously at the Ice-CVI and total inlet. It is easily seen that super-micrometer particles preferentially serve as IN but also sub-micrometer particles larger than 300 nm acted as IN.

Beside the size information, findings about the chemical composition of IN were obtained. These studies were analytically restricted to particles larger than 100 nm, i.e. the results can be attributed to residues acting as IN and are hardly influenced by residues from secondary generated ice particles.

Average black carbon (BC) mass concentrations of the ice particle residues were derived from a particle soot absorption photometer (PSAP). They varied between 0.3 and 1.9 ng $m^{-3}$ for the cloud events during CLACE 4 which was only 2 – 3 % of the totally abundant BC in the background aerosol particles (15 – 60 ng $m^{-3}$). However, when inferring a BC mass fraction in the IN (by relating its mass to the total residual mass inferred from the SMPS results) an enrichment of BC with respect to the background aerosol particles could be found (Fig.3).

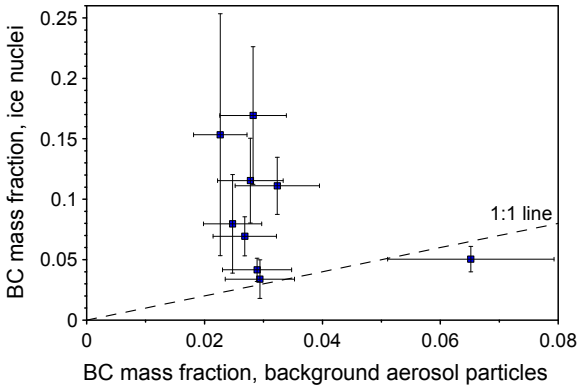


***Fig.3:*** *Scatterplot of BC mass fractions derived for ice nuclei and background particles sampled simultaneously with the Ice-CVI and total inlet, respectively. The dotted line indicates the 1:1 relation.*

This enrichment suggests that BC plays an active role in heterogeneous ice nucleation or is related to another ice forming aerosol compound [Cozic et al., 2008].

Another indication of an anthropogenic influence on heterogeneous ice nucleation in the lower troposphere was observed with a high-resolution, time-of-flight aerosol mass spectrometer (HR-ToF-AMS). In the ice particle residues only the hydrocarbon-like organic compound ($C_3H_7^+$) that has primary anthropogenic sources but hardly any secondary generated oxygenated organic compound ($C_2H_3O^+$) was detected in contrast to the background aerosol particles (Fig. 4).

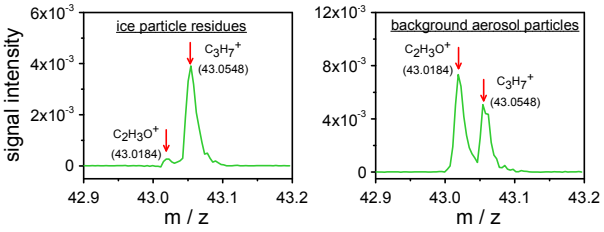


***Fig.4:*** *Relative contributions of hydrocarbon-like and oxygenated organic aerosol particles to the ice particle residues and background particles.*

Since the importance of the particle ice nucleating capability is mainly a number and not a mass related phenomenon one main effort was to couple single particle analyzing techniques to the Ice-CVI to permit the analysis of single ice nuclei. Hence, two in-situ aerosol mass spectrometers, the single particle laser ablation time-of-flight spectrometer (SPLAT) and an aerosol time-of-flight mass spectrometer (ATOFMS) and an impactor for off-line analysis with an environmental scanning electron microscope were connected to the Ice-CVI. Results of the SPLAT measurements are illustrated in Fig.5. The pie charts show the percentage of particles (regardless of the particle size) that belong to different particle groups. It is evident that the IN composition differs strongly from the background aerosol composition. Mineral dust is by far the dominating substance in the ice particle

residues. But also organic/carbonaceous particles were present whereas sulfate is depleted compared to the background particles.

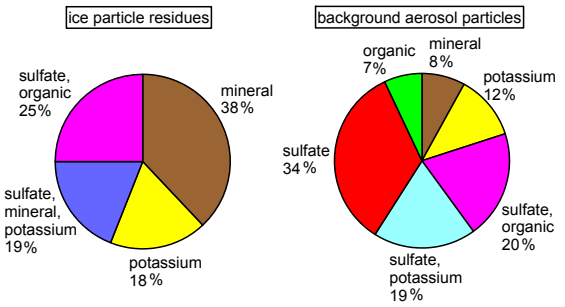


***Fig.5:*** *Relative distribution of different particle classes in background aerosol particles and in ice particle residues obtained from single particle SPLAT measurements.*

These findings were supported by mass size distribution results from the ATOFMS (Fig.6) and by the analysis of ice particle residue impactor samples (Fig.7) with ESEM.

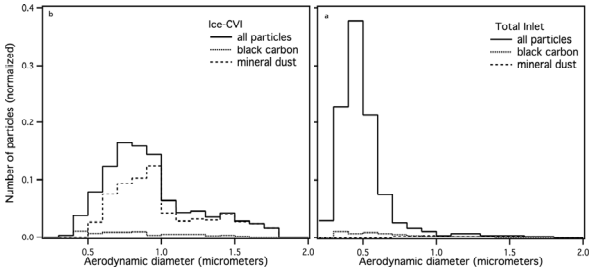


***Fig.6:*** *Comparison of mass size distributions of background aerosol (total inlet) and ice particle residues (Ice-CVI) measured with the ATOFMS.*

The ATOFMS results imply that almost all super-micrometer IN are mineral dust particles whereas in the sub-micrometer size range there are still some unidentified residues. With respect to the background aerosol mineral dust and BC particles are enriched in the ice particle residues, the latter verifying the bulk aerosol results obtained from the PSAP (cf. Fig.3).
Qualitatively the ESEM analysis yields similar results. The large ice nuclei are dominated by mineral dust (Si) but carbonaceous (C) particles are found for the smaller ones above 200 nm.

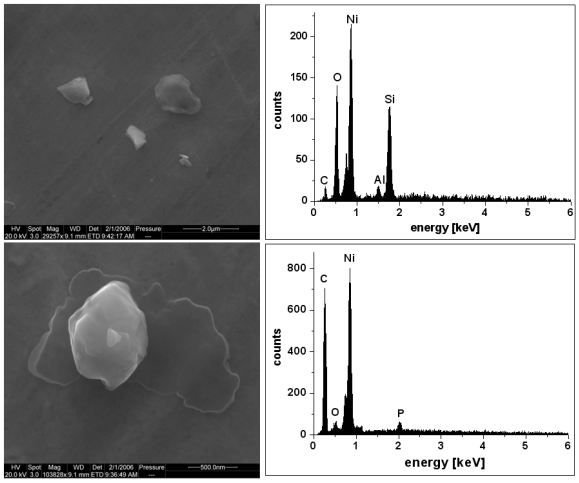


***Fig.7:*** *Secondary electron image and EDX spectrum of ice particle residues. The Ni peak is caused by the substrate.*

During CLACE 6 the IN chamber FINCH was connected to the Ice-CVI in order to activate the ice particle residues by deposition and condensation freezing to which IN counters are generally restricted to. FINCH could activate approximately only 1 of 100 residues implying that drop freezing processes like immersion, contact or evaporation freezing are much more important ice formation mechanism in the investigated lower tropospheric mixed-phase clouds.

## 5. CONCLUSION

By means of the novel Ice-CVI sampling system is was feasible to separate ice particle residues in scavenged or nucleated particles from secondary ice and true heterogeneously acting ice nuclei by their different size ranges. The latter have been chemically analyzed revealing that they are mainly mineral dust particles. Moreover, carbonaceous particles (organic, black carbon) have been identified in the IN but it needs to be further investigated whether they play an active role in heterogeneous ice nucleation or are at least related to

another ice forming aerosol compound not identified until now.
From the coupling of the Ice-CVI with an IN counter it is assumed that deposition and condensation freezing are not important ice forming processes in lower tropospheric mixed-phase clouds as long as super-cooled drops dominate the number of cloud particles.
It is intended to continue the investigation of ice formation in atmospheric clouds using the IfT CVI technology in cooperation with other research institutions within the German collaborative research centre “The tropospheric ice phase (TROPEIS)”, onboard the new German high altitude long range research aircraft HALO, and in lab studies at the Leipzig aerosol and cloud simulator LACIS.

## 6. ACKNOWLEDGEMENTS

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