

Aerosol Scavenging during the Early Growth Stage of Ice Crystal Formation

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Abstract

This paper investigated the possibility that aerosol particles are scavenged during the first and fast diffusional growth of small ice crystals. After ice phase formation, riming, scavenging and aggregation may lead to the collection of additional aerosol particles. Therefore, particles left after ice evaporation in hydrometeors, called ice residuals, may not currently be identical to ice nucleating particles. To overcome this problem, the largest ice crystals are removed during sampling in clouds and only crystals in the initial phase of growth, with diameters lower than 20 - 30 μm , are usually considered. Published papers assume that no aerosol scavenging takes place during the initial phase of growth of small ice crystals. The aim of this paper was to ascertain if this assumption is valid. Experiments were performed in a cold laboratory by considering ice crystals growing in the presence of supercooled droplets. Results showed that crystals can scavenge aerosol even in the first stage of growth. Theoretical considerations show that aerosol scavenging cannot be explained by Brownian diffusion, inertial impaction or interception processes. We suggest that the presence of aerosol in the pristine ice crystals may be due to diffusiphoretic force. During diffusive crystal growth, a flow called Stefan's flow exists near the hydrometeor surface, driving the nearby aerosol particles towards the surface of the growing hydrometeors.

Keywords

Ice Crystals, Ice Nucleating Particles, Aerosol Scavenging, Diffusiophoresis

1. Introduction

Ice can form homogeneously or heterogeneously through primary processes (nucleation from liquid or water vapour phases) if ice nucleating particles (INPs) are present. In addition, secondary processes can produce ice crystals in the

presence of pre-existing ice without the action of INPs [1]. Droplets freeze spontaneously at a temperature of -38°C , whereas haze droplets freeze at lower temperatures [2]. In the presence of INPs, ice formation initiates at a higher temperature than homogeneous nucleation in a variety of ways: deposition, condensation freezing, immersion freezing and contact freezing.

Substances have different freezing efficiency depending on the nucleation modes (deposition, condensation/immersion freezing), further hindering our understanding of ice formation. INP concentration can be measured in a variety of ways, in the laboratory or in the field, using on-line (such as mixing or continuous flow diffusion chambers) or off-line instruments (particles are collected on a substrate, and subsequently exposed to controlled conditions, or in a liquid through an impinger). A summary of laboratory and portable instruments used to study ice nucleation can be found in Cziczo *et al.* [3]. Small pristine ice crystals can derive from direct deposition of vapour on aerosol particles, or from freezing of supercooled droplets (homogeneously or heterogeneously) followed by growth, due to vapour diffusion or collection of liquid droplets (riming).

Heterogeneous ice nucleation requires only a single aerosol particle for each cloud droplet or ice crystal. After ice formation, additional processes can introduce aerosol particles into the ice crystal (e.g. riming, scavenging). Uptake of gases on ice crystals may also take place [4] [5]. Furthermore, ice crystals formed through droplet freezing may contain cloud condensation nuclei material. Therefore, particles remaining after evaporation of each crystal (ice residual) and the original INP cannot currently be assumed to be identical. To overcome this problem, the largest ice crystals are removed during samplings in mixed-phase clouds and cirrus, and only crystals with diameters lower than 20 - 30 μm are considered, assuming that no aerosol scavenging exists during the initial phase of growth by water vapour diffusion [3] [6].

Particles located in ice crystals were directly identified off-line in the past through formvar (FV) replicas of precipitating crystals and particle analysis using electron microscope techniques [7] [8] [9]. In the early 1990s efforts were made to understand the nature of INPs by aircraft using a counter flow virtual impactor (CVI) to separate ice crystals from other solid/liquid components (interstitial particles, supercooled droplets, etc.) of mixed-phase clouds [10]. The ice crystals were then sublimated and the residual particles collected for off-line analysis. Artefacts were disclosed by the collision of ice crystals with aircraft and CVI inlet surfaces [11].

Since the early 2000s, the most common technique used in aircraft-based studies has been on-line real-time mass spectrometry based on the analysis of residual particles after evaporation of ice crystals [12] [13] [14]. To extract small ice crystals (diameter in the range 5 - 20 μm) from mixed phase clouds, Kupiszewski *et al.* [6] employed an evaporation tube to remove supercooled droplets and a pumped CVI to remove interstitial particles and residual particles released from the droplets in the evaporation unit. The aim of this paper is to ascertain if ice

crystals scavenge aerosol during water vapour diffusion even in the initial phase of growth.

2. Experiments

The experimental facility consisted of a plexiglass cylinder (12 cm in diameter, 140 cm in height), placed in a cold room at about -14°C and at atmospheric pressure (**Figure 1**).

The aerosol was generated in a neighbouring room at $T = +5^{\circ}\text{C}$ by nebulizing a suspension of Arizona Test Dust (ATD, 0 - 3 μm Powder Technology Inc.) in Milli-Q water ($10\text{ g}\cdot\text{L}^{-1}$) by means of a one-jet Collison nebulizer (BGI). After the atomizer, the droplets were evaporated by a drier made of silica gel. We used ATD simply because it is an insoluble aerosol. It does not matter if the chosen aerosol is a good ice nucleus or not. A soluble aerosol (e.g. NaCl) would change diameter due to deliquescence and influence the water vapour gradient.

The size distribution of the generated aerosol (**Figure 2**) was measured in separated runs with a Long Vienna U-Type DMA (L-DMA model 5400, CPC model 5403, Grimm Aerosol Technik) at the bottom of the cylinder in the absence of droplets, five minutes after the end of the generation. The aerosol particle number concentration was $(2.1 \pm 0.8) \times 10^4\text{ cm}^{-3}$.

Milli-Q liquid droplets were produced using an ultrasonic nebulizer and were sampled at the bottom of the column with an Optical particle Counter (OPC, Grimm Aerosol Technik, mod. 1.108). **Figure 3** shows the measured droplets size distribution. The droplets concentration was in the range $600 - 1000\text{ cm}^{-3}$ and the average diameter was $7.0\text{ }\mu\text{m}$.

The procedure followed in each run can be summarized as follows. Filtered air flowed inside the column for five minutes in order to remove particles. Afterwards,

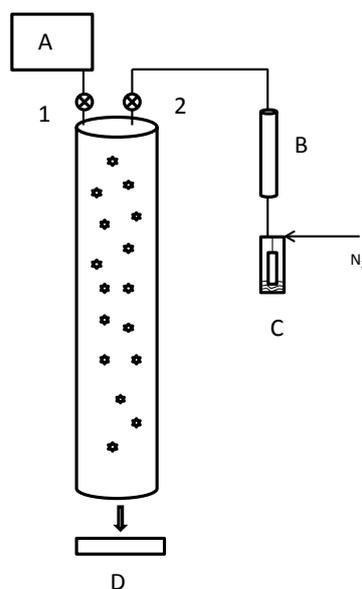


Figure 1. Schematic of the experimental facility. A: Droplet generator; B: Silica gel column; C: Collison atomizer; D: Ice crystal collector.

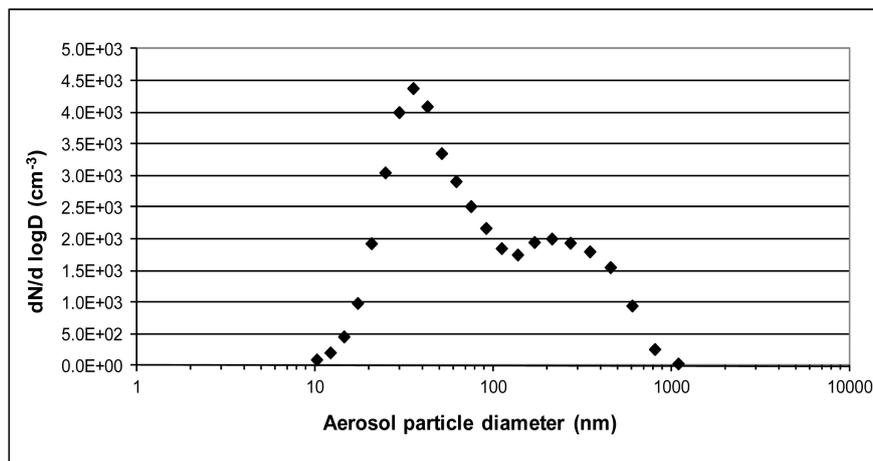


Figure 2. Size distribution inside the column of the generated ATD aerosol.

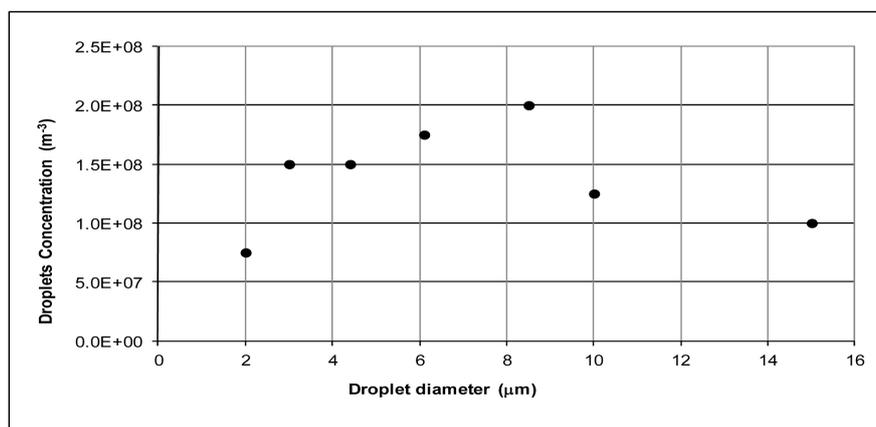


Figure 3. Size distribution of the droplets measured at the bottom of the column.

aerosol particles were injected at the top of the column (valve 2 open, **Figure 1**) for six minutes ($1.4 \text{ L}\cdot\text{min}^{-1}$ flow rate). During this step the small hole placed at the bottom of the column was left open. After about five minutes Milli-Q liquid droplets produced by the ultrasonic nebulizer were introduced at the top of the column for about 15 s (valve 1 open, **Figure 1**). Afterwards the column was closed. The droplets became supercooled in a few seconds. During the short period after injecting droplets and nucleation (15 s time of injection and 20 s nucleation time) we did not observe wall icing. After each run we purged the column with dry gas air for ten minutes.

The ice nucleation was activated by briefly inserting (2 - 3 s) at the top of the cylindrical column the tip of a small metal wire previously cooled by immersion in a Dewar holding liquid nitrogen. The ice nucleation with wire concerns only droplets held in a very small volume (1 - 2 cm³), but in a time of the order of 20 s the droplets in the whole column evaporated and only ice crystals were observed. The number of ice crystals generated in a very small volume at the top of the column, where nucleation is activated through a small metal wire, is negligible with respect to the number in the full column, which has a volume of 15.8 L.

We explain these results by claiming that later ice crystals come from supercooled droplets rapidly evaporating in the presence of the initial few ice crystals, due to the difference in saturation vapour pressure over water and ice (Wegener-Bergeron-Findeisen process). The droplets cool sufficiently to freeze homogeneously even at an initially high temperature (about -14°C). Therefore, the continuous process of new ice crystal formation and growth can explain the fast disappearance of the droplets and the very high increase in ice crystal concentration. The presence of small ice crystals in the unstable system (supercooled droplets) appears to trigger the nucleation process in the whole liquid cloud [15].

In separate runs we introduced in the column ATD aerosol and droplets without performing nucleation. Both visual observation of the lighted column and sampling on stubs covered with formvar confirmed the presence of only droplets and ruled out the presence of crystals. Therefore, heterogeneous nucleation (immersion and contact freezing modes) did not occur in the chosen experimental conditions.

Ice crystals were sampled and replicated with the technique described by [16]. Precautions need to be taken during ice crystal collection to avoid inaccurate replicas [17]. The crystals (prevalently hexagonal plates) were collected at the bottom of the column on SEM specimen mounts. The stubs were previously prepared by placing a small piece of double-coated carbon conductive tape on them, covered by a small piece of a glass microscope slide. Before starting crystal sampling, the glass was covered with a thin layer of FV dissolved in chloroform (2%), and subsequently exposed to the falling crystals. The free falling crystals settled on the FV surface with the most developed face. Exposure time was about 10 s. The slides were then quickly placed inside a small box filled with silica gel, where crystals and chloroform evaporate. An example of the replica of the sampled crystals at the bottom of the column is given in **Figure 4**. A rough estimation of the ice crystal concentration can be obtained by counting the number of ice crystals sampled on stubs covered with formvar, and by considering the sampling area, sampling time and average sedimentation velocity of the crystals. An ice crystal concentration of the order of 500 cm^{-3} can be obtained.

The temperature during tests (about -14°C) was measured with a Pt-100 inserted near the wall of the column, and the relative humidity by a dew point hygrometer. Temperature and humidity were measured in separate runs by generating droplets and introducing them in the column for the same time as for the complete run (15 s). Before nucleation started, the air in the column was found to be saturated with respect to the water.

The liquid water content (LWC) was measured in separate runs by generating droplets for 15 s and by sucking supercooled droplets at the bottom of the column on the surface of cooled impactor. The droplets froze instantaneously. The ice deposit was then transferred into a small plastic cylinder and weighed with a precision balance. LWC was $(0.5 \pm 0.1)\text{ g}\cdot\text{m}^{-3}$ averaged on three runs. In order to

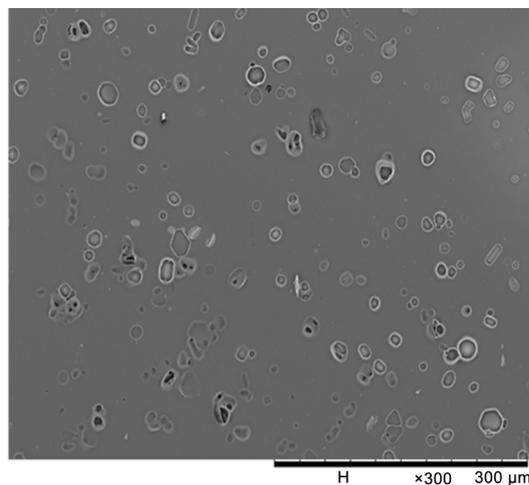


Figure 4. Replica of crystals sampled on stub covered with formvar.

check if droplets scavenge aerosol before ice nucleation, experiments were also performed with the procedure outlined above, but in the absence of ice nucleation. Droplets were sampled with the same technique as ice crystals, and aerosol scavenging from droplets was not observed.

3. Results

Ice crystals collected at the bottom of the column on stubs (**Figure 4**) were gold shadowed and investigated under SEM.

Most of the crystals were completely covered with the FV, precluding identification of scavenged aerosol as SEM cannot penetrate the FV. This is seen in **Figure 5(a)** and **Figure 5(b)**, where ATD particles are clearly visible inside the crystals when FV does not cover the crystal, whereas they are difficult to see or not observed when FV covers the crystal.

In our tests, the number of crystals not covered by FV represented a small fraction of the total replicas observed and only a fraction of crystals showed aerosol particles. We examined 102 crystals (10 - 30 μm range diameter) showing ATD scavenged aerosol in the range 140 - 1100 nm. We did not consider particles smaller than 140 nm due to difficulty in their unambiguous identification.

Figure 6 shows the average number of ATD particles found per each examined crystal vs. the mean aerosol diameter in each size bin considered, and estimated by the theoretical values given by Brownian diffusion, impaction and interception. The experimental data were obtained by observing ice crystal replicas at SEM and measuring the number and size of the scavenged particles. The number of collected particles obtained from the experimental runs for each crystal was on average 6.5. The highest average concentration of ATD in the crystals examined concerned particles with a diameter of 400 nm.

We deployed Fuchs' formula [18] for the interception and Brownian diffusion scavenging efficiencies, and Park *et al.*'s formula [19] for impaction (**Table 1**).

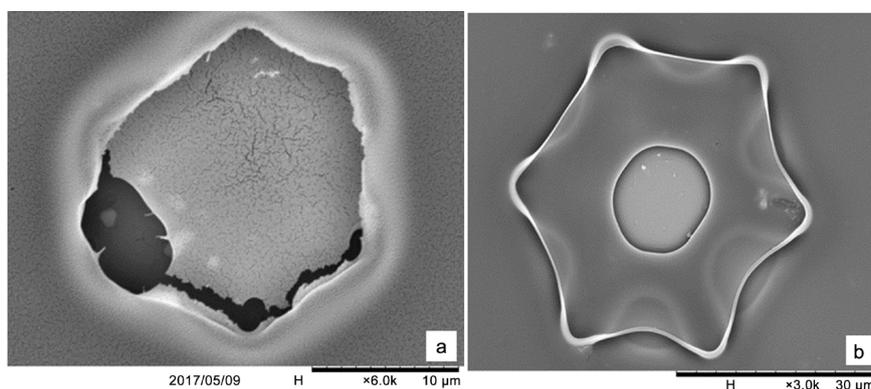


Figure 5. Ice crystal replicas partially covered with formvar.

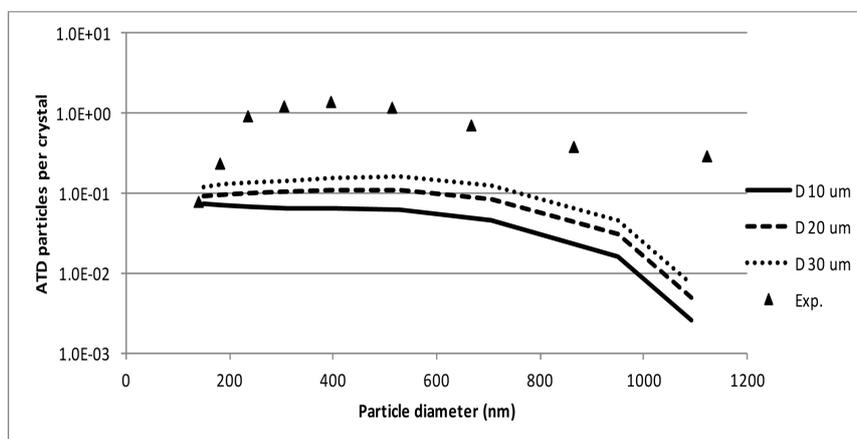


Figure 6. Number size distribution of aerosol particles scavenged on average per examined crystal experimentally observed (Exp.), and theoretically given by impaction, diffusion and interception for three different crystal diameters (10, 20 and 30 μm).

Table 1. Semi-empirical correlations to calculate the elementary collection efficiencies due to different mechanisms: E_I capture efficiency due to interception, E_D due to Brownian diffusion and E_{IMP} due to impact.

Scavenging mechanisms	Equation	Reference
Interception	$E_I = 3I$	Fuchs, 1964, pg. 165
Brownian diffusion	$E_D = 4.03 \text{ Pe}^{-2/3}$	Fuchs, 1964, pg. 210
Impaction	$E_{IMP} = [\text{Stk}/(\text{Stk} + 0.35)]^2$	Park <i>et al.</i> , 2005

In **Table 1**

$$I = \frac{d_{\text{aer}}}{d_{\text{crystal}}} \quad \text{Pe} = \frac{d_{\text{crystal}} U_{\text{crystal}}}{D_{\text{diff}}} \quad \text{Stk} = \frac{\rho_p d_{\text{aer}}^2 U_{\text{crystal}}}{18\mu d_{\text{crystal}}}$$

where: d_{aer} is the aerosol diameter; d_{crystal} is the crystal diameter; U_{crystal} is the crystal fall velocity; D_{diff} is the diffusion coefficient of aerosol particle, ρ_p is the particle density and μ is the dynamic viscosity of the gas.

Calculations were carried out by considering the measured concentration and size distribution of the aerosol in the same range used to evaluate the scavenged

experimental particles, and by assuming that crystals fall from the top to the bottom of the column (140 cm long) by maintaining a constant diameter. Crystals with a diameter of 10, 20 and 30 μm falling at terminal velocities of 0.35, 1.25 and 2.15 $\text{cm}\cdot\text{s}^{-1}$, respectively [20] were considered. The number of particles theoretically collected by crystals with 10, 20 and 30 μm diameter was 0.47, 0.73 and 1.02 respectively, *i.e.* about one order of magnitude lower than experimental values.

We rule out that crystals can be charged as ice crystal growth is due to water vapour diffusion of evaporating distilled water droplets in the absence of an external electric field, riming process or ions, which could determine a charge of the crystals. Images of sampled crystals show no aggregation. Separate measurements of ATD aerosol charges were carried out by means of an electrostatic precipitator with an electrostatic field of 8 $\text{KV}\cdot\text{cm}^{-1}$. The electrostatic precipitator affected aerosol number concentration less than 10%.

Figure 7 shows a few crystal replicas showing scavenged ATD particles.

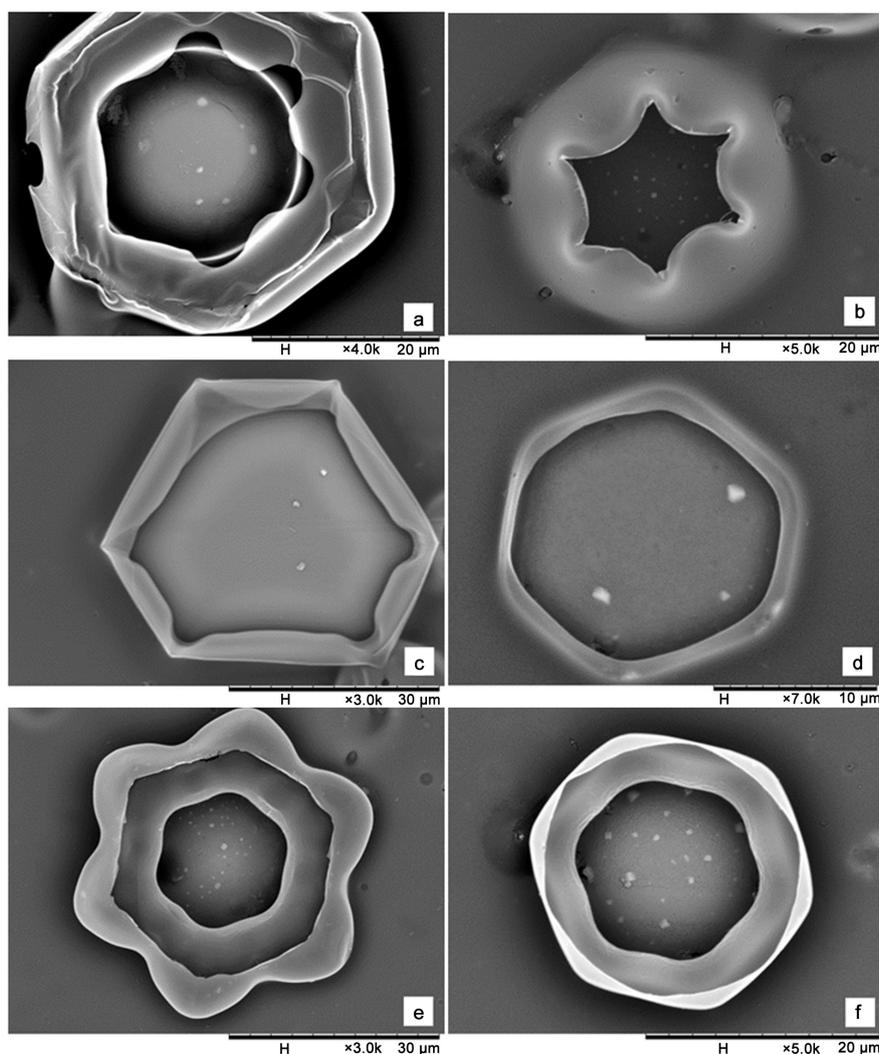


Figure 7. Ice crystal replicas showing scavenged ATD aerosol particles (a)-(f).

Microanalysis (Bruker, Quantax System) of particles scavenged by crystals sampled on FV-coated carbon specimen mounts was performed with an Environmental SEM (Zeiss, EVO LS 10). The presence of elements characteristic of ATD particles was confirmed (Si, Al).

4. Discussion

Our experiments showed that ice crystals with diameters of 10 - 30 μm scavenged aerosol in the early stage of growth. Possible artefacts, e.g. sedimentation of ATD on the stubs during crystal sampling (lasting a few seconds), were omitted from both the theoretical evaluation and experimental tests. Stubs placed at the bottom of the column for a period of 10 s after the introduction of aerosol in the column and in the absence of nucleation did not sample ATD particles.

Our laboratory experiments show that the scavenging due to Brownian diffusion, impaction, and interception cannot account for the scavenged aerosol observed. We left out aerosol scavenging due to electrostatic force as ice crystals and aerosol were uncharged. We suggest that the presence of aerosol in the small crystals can be explained by diffusiophoretic force. During diffusive crystal growth a flow, called Stefan's flow, exists near the hydrometeor surface, exerting a force on the nearby aerosol particles towards the surface of the growing hydrometeors [21]. The diffusiophoretic velocity is almost independent of aerosol diameter [22] [23] [24].

At a temperature of -14°C the difference in saturation vapour pressure over water and ice peaks and consequently the crystal growth rate is at a maximum. By considering an ice crystal at $T = -14^\circ\text{C}$, the air being saturated with respect to ice on its surface, and saturated with respect to water at about 40 μm from the centre of the crystal [25], the diffusiophoretic velocity is about $100 \mu\text{m}\cdot\text{s}^{-1}$, from Goldsmith and May, eq. 4 [26]. Following our laboratory results, scavenged aerosol in mixed/cold clouds could be present even in small ice crystals formed via deposition, or via homogeneous freezing followed by growth through water vapour diffusion.

Previously published papers assume that small crystals do not scavenge aerosol during early growth, as only impaction and riming are considered as possible mechanisms. The possibility that crystals can scavenge aerosol during diffusive growth is discarded, and consequently it is assumed that small ice crystals are representative of the original INP [3] [27] [28] [29] [30].

Few papers report experimental results which could confirm our laboratory findings. By considering papers published long ago [31] [32] [33], it was found that many unrimed ice crystals sampled at the South Pole contained particulate matter other than that of the central nucleus. This implied that these crystals collected particulate matter during their growth. Goodmann *et al.* [34] sampled and replicated Antarctic stratospheric ice crystals (average diameter 5 - 16 μm) and observed a high density of sub-micron particles on the crystal faces. Laboratory experiments [35] [36] highlighted the importance of phoretic forces during

crystal growth. A recent paper [37] showed aerosol particles in small ice crystals (Figure 8) collected at Dome C-Concordia site (located on the Antarctic plateau; 3233 m a.s.l.), that could not be accounted for by Brownian diffusion, inertial impaction or interception processes (Figure 8).

Cziczo *et al.* [38] conducted aircraft measurement campaigns within regions of high cirrus cloud abundance over North and Central America and nearby oceans. Mineral dust was the most dominant heterogeneous ice nucleus. The freezing mechanism was heterogeneous in 94% of cloud encounters. Homogeneous freezing was inferred in only two distinct clouds with about 15% mineral dust and metallic particles. The presence of these particles even in the events classified as “homogeneous freezing” could depend on aerosol scavenging following homogeneous nucleation.

At Jungfraujoch station (February/March 2006, CLACE 5), Ebert *et al.* [39] found particle groups significantly enriched in IRs (Pb-bearing particles, C-O-S particles and complex mixtures) with respect to background aerosol. A depletion was measured for the soluble particle group sulphate (from 36% to 15%) and sea-salt (from 19% to 8%). The temperature during the experiment was in the range -27°C to -12°C . Significant numbers of all clouds observed were mixed-phase clouds. As biological material was not found, the immersion freezing of droplets containing both INP and soluble compounds should be unlikely at the higher experimental temperatures [40] [41]. Ice crystals could be formed from the freezing of droplets containing only uncoated dust particles and soluble compounds (e.g. sulphate) should be scavenged during crystal growth.

The presence of soluble compounds in IRs has been reported in several published papers [42]. Examining residuals of 5 - 20 μm ice crystals in mixed phase cloud events during CLACE 6 and INUIT campaigns at the Jungfraujoch, Kamphus *et al.* [43] and Schmidt *et al.* [30] found that many of the IRs showed soluble compounds. The possibility of a salt/soluble compounds scavenging process after ice activation was also recognized by the authors, even if it was not attributed directly to diffusiohoresis. We note that homogeneous freezing cannot take place at the temperatures measured during the campaigns.

Worringen *et al.* [44] in a joint field campaign (January-February 2013,

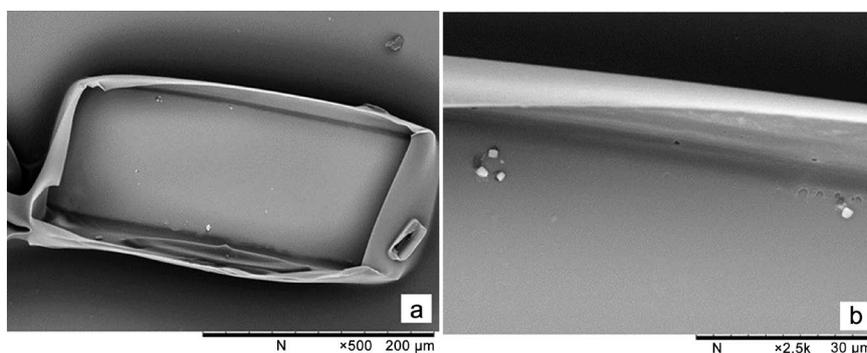


Figure 8. (a) Ice crystal replicated at Dome C on 21 June 2012; (b) Magnification of aerosol scavenged from a hollow column.

Jungfraujoch, Switzerland) also observed considerable amounts (median abundance mostly a few percent) of soluble material (e.g., sea-salt, sulphates). As these compounds are not expected to act as INPs at the temperatures considered, the authors could not explain the results and considered the soluble particles instrumental contamination artefacts. However, we note that the supposed “artefacts” should concern all three different techniques used in their research, and this appears to be unlikely.

A contribution to clarify the question was given by Pratt *et al.* [45], who used a continuous flow diffusion chamber (CFDC) to reprocess the residual particles of crystals sampled in orographic wave clouds at high altitude over Wyoming. They found that the number concentrations of cloud residual particles exceeded CFDC ice nuclei number concentrations by an order of magnitude on average, indicating extra non-nucleation-related scavenging of particles. This could mean that during growth the crystals scavenged aerosol particles with low nucleating efficiency. By comparing the chemical composition of IRs (Figure 2 of their paper), the percentage of soluble compounds (NaCl/KCl) was much higher than in clean air (Figure S-4 of their paper).

Some authors rule out the possibility of aerosol scavenging during vapour water diffusion growth of crystals on the basis of the agreement between the number of residual particles and the number density of cirrus crystals measured with an ice detector [6] [10] [29] [46]. However, we note that strictly speaking the agreement between ice crystal and residual number concentrations does not mean scavenging processes are absent, as particles may aggregate forming a unique particle during crystal evaporation in the sampling system [47] [48].

5. Conclusions

This paper investigated the aerosol scavenging of aerosol (ATD) during the early growth of ice crystals due to water vapour diffusion. Aerosol scavenging was measured in a cylindrical column placed in a cold room at about -14°C and at atmospheric pressure. The aerosol was generated by flowing filtered air through a Collison immersed in a suspension of ATD. After the atomizer, the droplets were evaporated by a drier made of silica gel. Liquid droplets of Milli-Q water, produced using an ultrasonic nebulizer, were introduced at the top of the column for 15 s, spread in the whole column and became supercooled in a few seconds.

The ice nucleation was activated by briefly inserting at the top of the cylindrical column the tip of a small metal wire previously cooled by immersion in a Dewar holding liquid nitrogen. In a period of the order of 20 s the droplets evaporated in the whole column and only ice crystals were observed. Rapidly evaporating droplets in the presence of ice crystals cooled down and homogeneously froze. The continuous process of ice crystal nucleation and growth can explain the fast disappearance of the droplets and the very high increase in ice crystal concentration.

Ice crystals were replicated at the bottom of the column through a solution of FV and examined at SEM. We restricted our research on scavenging of aerosol to crystals smaller than 30 μm , *i.e.* crystals which are usually considered not to scavenge aerosol during water diffusion growth through Brownian diffusion, inertial impaction and interception processes.

The number of particles theoretically collected by crystals with 10, 20 and 30 μm diameter, were 0.47, 0.73 and 1.02 respectively. The number of collected particles obtained from the experimental runs for each crystal was on average 6.5, *i.e.* about one order of magnitude higher than the theoretical value. The key finding of this experiment, inferred from SEM investigation, is that even small crystals can scavenge aerosol and we suggest that this is due to Stefan's flow. Papers published long ago [31] [32] [33] and more recent studies [30] [39] [40] [41] [44] seem to support our conclusions. The obtained results demonstrate that the identification of IRs and INPs may not be valid, even considering small ice crystals (<30 μm). Therefore, additional experiments are required to expand our knowledge of the scavenging processes in the atmosphere, mainly in the initial phase of ice crystal growth.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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