

Ice nucleation ability of aged aerosol particles under cirrus conditions

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Abstract

Cold, high-altitude cirrus clouds, which consist entirely of ice crystals, play an important role in the Earth's radiation budget. They form either through homogeneous freezing of aqueous solution droplets, or through heterogeneous ice nucleation on a small subset of atmospheric aerosol particles known as ice-nucleating particles (INPs). INPs lower the energy barrier for ice formation, enabling ice nucleation at lower supersaturations and warmer sub-zero temperatures. Freshly emitted or formed INPs undergo substantial physical, morphological, and chemical aging through a variety of processes, including internal mixing through vapor condensation, surface and structural changes during ice cloud processing, and chemical modification through reactive uptake of precursor gases. These aging pathways have the potential to profoundly alter the ice nucleation ability of INPs, and there is still ample scope for in-depth experimental studies of these processes and their representation in atmospheric models for cirrus cloud formation.

This thesis took an experimental approach to investigating the influence of three key aging pathways on the ice nucleation ability of atmospherically relevant INPs under cirrus conditions. The experiments were carried out at two large-scale cloud chamber facilities: the Aerosol Interaction and Dynamics in the Atmosphere (AIDA) facility at the Karlsruhe Institute of Technology (KIT), and the Cosmics Leaving Outdoor Droplets (CLOUD) facility at the European Organization for Nuclear Research (CERN). The two cloud chambers were used to simulate atmospheric aging at low temperatures over long timescales, offering extensive instrumentation to resolve the chemical and structural changes of the INPs during aging. Meanwhile, the ice nucleation ability of the particles was continuously measured using Continuous Flow Diffusion Chambers (CFDCs).

The first aging mechanism investigated was **internal mixing** by condensation of organic and inorganic precursor vapors onto primary aerosol particles, particularly K-feldspar particles as a proxy for mineral dust. It was found that the intrinsic heterogeneous ice nucleation ability of the K-feldspar particles was completely masked by a large number of coating types, including aqueous sulfuric acid, aqueous nitric acid, and viscous secondary organic material (SOM) from the oxidation of isoprene. A novel aspect of this thesis was the neutralization of acidic nitrate and sulfate coating layers by ammonia. In the case of ammonium nitrate, this led to the reappearance of a heterogeneous ice nucleation mode because the K-feldspar particles triggered the heterogeneous crystallization of the coating layer, which by itself then acted as

the ice nucleating entity. However, no heterogeneous ice nucleation was observed in the case of ammonium sulfate, presumably due to the absence of heterogeneous crystallization of the coating layer.

The second mechanism studied was the **morphological aging** of secondary organic aerosol (SOA) particles from isoprene oxidation during ice cloud processing. Through a complex sequence of processes, including liquefaction of the organic material, homogeneous freezing, re-vitrification of the organic material within the ice lattice, and sublimation of ice, the initially compact SOA particles transformed to irregularly shaped particles with internal cavities and pores. Although having a much larger surface area and potential sites to promote ice formation via the pore condensation and freezing (PCF) mechanism, these ice cloud processed SOA particles were found to be only marginally better INPs than their pristine, unprocessed counterparts. This finding corroborates previous experiments conducted with SOA particles from α -pinene oxidation and suggests that, irrespective of their history, pure SOA particles are generally poor INPs under cirrus conditions. However, ice cloud processing may be relevant for SOM-coated INPs, as it can disrupt an initially uniform coating layer, thereby re-exposing active sites that were previously shielded.

The third set of experiments investigated **chemical aging** mechanisms by exposing two types of seed particles, i.e., sulfuric acid solution droplets and ammonium sulfate crystals, to either glyoxal or isoprene, both under dark and UV-illuminated conditions. In the case of the chemically processed sulfuric acid solution droplets, mass spectrometry revealed the presence of glyoxal-related particle-phase fragments or isoprene-derived oxidized organic material, but these did not alter the homogeneous freezing mode of the seed particles. In the case of crystalline ammonium sulfate seed particles with an intrinsic heterogeneous ice nucleation ability, chemical aging produced different results depending on the type of organic precursor. A coating of isoprene-derived SOM deactivated the seed particles. Reactive glyoxal uptake led to the formation of organonitrogen and imidazole-related compounds. These altered the surface or near-surface properties of the ammonium sulfate crystals during early-stage carbonyl-ammonium chemistry, thereby transiently enhancing the seed particles' ice nucleation ability.

Overall, the results demonstrate that the ice nucleation ability of pristine INPs does not change in a consistent manner as a consequence of aging. The ice nucleation activity of aged aerosol particles is influenced by coating composition, phase state, cloud-processing history, and chemical reactivity, which can cause it to increase or decrease compared to the unprocessed, pristine particles. Incorporating these complex effects of aerosol aging into atmospheric models is challenging but ultimately necessary to improve predictions of cirrus cloud formation.

Preface

The PhD candidate confirms that the scientific content, interpretation of results, and final decisions regarding the material presented in this thesis are her own, following discussions with the supervisory team and collaborators.

ChatGPT (<https://chat.openai.com/>) was used to improve Python code for plotting scripts, as well as for stylistic improvements in the thesis.

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1 General scientific background

Clouds form an important part of the Earth's atmosphere and play a dominant role in the Earth's radiation budget and hydrological cycle, thereby helping to regulate the global average temperature. This thesis aims to improve our understanding of how clouds form, with a particular focus on cirrus clouds. These high-altitude clouds consist entirely of ice crystals, which can originate from the outflow of deep convection, but can also form in situ in the upper troposphere at low temperatures less than 235 K. The formation of these ice clouds is influenced not only by thermodynamic conditions, such as temperature and relative humidity (RH), but also requires the presence of particular seed particles stemming from the large family of atmospheric aerosol particles.

To provide context for the topic of this thesis within the broader scientific landscape, Section 1.1 therefore begins with an overview of atmospheric aerosol particles, detailing their sources, composition, size, lifetime, and interaction with clouds. Section 1.2 then introduces the various pathways by which ice crystals can form in the atmosphere, the so-called ice nucleation modes. This is followed by a discussion of the multiple research approaches that have been employed in the field of ice nucleation so far, including large-scale chamber experiments, which can play an important role in bridging the gap between field observations and modeling studies (Section 1.3).

Aerosol particles undergo continuous chemical, physical, and morphological transformations during their atmospheric lifetime, through processes collectively referred to as atmospheric “aging”. As the title suggests, this thesis focuses specifically on the ice nucleation ability of such aged aerosol particles. Section 1.4 therefore provides a brief overview and categorization of important atmospheric aging mechanisms. Section 1.5 subsequently emphasizes that, as a consequence of the aforementioned aging processes, aerosol particles that reach the upper troposphere – and thus relevant seeds for in situ cirrus formation – are complex, internally mixed particles which bear less resemblance to pristine, source-specific species. The chapter then concludes with a synopsis of the specific research questions and the methodological approach that have been employed in this thesis: a realistic simulation of important atmospheric aging mechanisms in large-scale cloud chamber experiments, and investigating how these aging processes affect the efficiency with which the aged aerosol particles can act as seeds for cirrus cloud formation (Section 1.6).

1.1 Atmospheric aerosols

Atmospheric aerosols are suspensions of solid or liquid particles in the gaseous phase of the atmosphere. They span a broad size range, from a few tens of nanometers to several tens of micrometers, and may occur as monodisperse systems with uniform particle size or, more commonly in the atmosphere, as polydisperse systems with a broad size distribution.

Atmospheric aerosol populations are typically described by particle size distributions, which are generally multi-modal rather than continuous (Seinfeld et al., 2012; Whitby, 1978). These characteristic modes reflect distinct formation and removal processes (Whitby, 1978). Newly formed particles usually fall within the size range of 1 nm to 10 nm and are therefore commonly associated with particle formation events. Aitken mode particles (roughly 10 nm to 100 nm) are commonly produced by new particle formation and combustion. Accumulation mode particles (roughly 0.1 μm to 1 μm) arise mainly from condensational growth and coagulation, while coarse mode particles ($> 1 \mu\text{m}$) are typically generated by mechanical processes such as mineral dust emission, sea spray, and biological release (Boucher et al., 2013; Seinfeld et al., 2012). The relative contribution of each mode varies with source region, meteorological conditions, and atmospheric processing. Overall, the nucleation and Aitken modes dominate particle number concentrations, whereas the accumulation and coarse modes contribute most strongly to aerosol surface area and mass loading.

Based on their formation pathways and sources, atmospheric aerosols are commonly classified as primary or secondary, and as natural or anthropogenic. Primary aerosols are directly emitted into the atmosphere from their sources and include particles such as sea salt, mineral dust, black carbon, and pollen (Seinfeld et al., 2012). Once emitted, these particles undergo continuous physicochemical transformations, including coagulation, condensation of vapors, cloud processing, and removal by precipitation (Poeschl, 2005; Seinfeld et al., 2012). Mineral dust particles are among the most abundant types of atmospheric aerosol (Kok et al., 2023; Textor et al., 2006). They originate predominantly from arid and semi-arid regions, where strong surface winds mobilize soil particles from major deserts such as the Sahara, Taklamakan, and Gobi (Prospero et al., 2014; Shao et al., 2013). These dust particles can be transported over long distances and are frequently observed to cross entire ocean basins.

Sea spray aerosols represent another major natural aerosol source and are generated through bubble-bursting processes at the ocean surface (Leeuw et al., 2011). Air–sea interactions produce particles that primarily consist of sea salt but may also contain organic matter, including residues of marine phytoplankton (O’Dowd et al., 2007). Biomass burning, particularly forest and vegetation fires, is a significant episodic source of aerosols, emitting large quantities of smoke particles that can be transported over continental and hemispheric scales (Andreae et al., 2001). Volcanic eruptions also contribute substantially to atmospheric

aerosol loading by injecting sulfur dioxide and ash particles composed of silica and feldspar minerals into the atmosphere (Textor et al., 2003). In addition, biogenic aerosols originate from terrestrial vegetation and forests and include biological particles such as pollen, spores, and bacteria (Després et al., 2012). Vegetation also emits large amounts of precursor gases that undergo atmospheric oxidation, leading to the formation of secondary organic aerosols (SOAs) (Hallquist et al., 2009).

Secondary aerosols are formed within the atmosphere through chemical reactions involving precursor gases rather than being emitted directly. Important examples include sulfate aerosols produced from the oxidation of sulfur dioxide and SOAs generated through the oxidation of biogenic or anthropogenic volatile organic compounds (VOCs). These secondary particles often form through nucleation and subsequent growth processes, significantly influencing aerosol number concentrations and size distributions (Kulmala et al., 2004). Anthropogenic activities and industrial emissions further contribute to secondary aerosol formation by releasing sulfur oxides, nitrogen oxides, ammonia, and organic vapors, which react to form sulfate, nitrate, and organic aerosol components.

In the atmosphere, aerosols from different sources interact with each other to form complex and dynamically evolving aerosol populations. These interactions and aging mechanisms, which are described in more detail in Section 1.4, are strongly influenced by aerosol lifetime. Depending on their size, composition, and altitude of origin, aerosol lifetimes can range from a few hours to several years. Long-range transport of aerosols has been widely observed, with mineral dust from major desert regions crossing oceans (Prospero et al., 2014; Riese et al., 2025), wildfire smoke spreading across hemispheres, and large volcanic eruptions, such as the 1991 Mount Pinatubo event, producing aerosol layers that persist globally for several years (Brasseur et al., 1992; Stenchikov et al., 1998; Stowe et al., 1992). These phenomena represent some of the longest-lived aerosol events observed in the Earth's atmosphere. Atmospheric aerosols are removed through dry and wet deposition processes. Dry removal mechanisms include gravitational settling of larger particles and the removal of smaller particles through Brownian diffusion and turbulent transport to the surface. Wet removal processes involve the interaction of aerosols with precipitation. Larger particles are efficiently removed by inertial impaction and collision with falling raindrops, whereas smaller particles may be scavenged through diffusion into cloud droplets or raindrops. Precipitation, therefore, plays a critical role in regulating atmospheric aerosol concentrations and contributes significantly to the cleansing of the atmosphere (Guo et al., 2016; Lelieveld et al., 2018).

Beyond their sources, transport, and removal, aerosols exert a profound influence on the Earth's climate system. Aerosols interact with incoming and outgoing radiation through scattering and absorption processes, collectively referred to as the direct radiative effect (Liu et al., 2014). Scattering aerosol particles generally induce a cooling effect at the surface,

whereas absorbing aerosol particles can lead to atmospheric heating (Ramanathan et al., 2001). This localized heating or cooling can modify cloud formation and cloud dissipation; this is known as the semi-direct effect of aerosols (Hansen et al., 1997). In addition, aerosols play a crucial role in cloud formation by acting as cloud condensation nuclei (CCN) and ice-nucleating particles (INPs). The microphysical properties of clouds formed in the presence of aerosols depend strongly on the characteristics of these particles, giving rise to the so-called indirect effects of aerosols on climate (Albrecht, 1989; Twomey, 1977). CCN are aerosol particles upon which supersaturated water vapor condenses to form cloud droplets, while INPs represent a much smaller subset of the aerosol particle population with specific surface properties that facilitate the formation of ice crystals by heterogeneous nucleation mechanisms (Vali et al., 2015). Through these direct, semi-direct, and indirect pathways, aerosols influence the Earth's radiation budget, hydrological cycle, and the complex aerosol–cloud–climate interactions that govern weather and long-term climate variability (Intergovernmental Panel on Climate Change (IPCC), 2023). Of the various cloud types in the atmosphere, cirrus clouds are among the most prevalent. Observations indicate that cirrus clouds occur frequently on a global scale and can reach occurrence frequencies of up to about 70 % in some parts of the tropics (Haladay et al., 2009; Sassen et al., 2008). Owing to their broad spatial coverage and strong impact on the Earth's radiation budget – resulting from their effective absorption of upwelling terrestrial radiation and strong reflection of incident solar radiation – understanding the aerosol-dependent pathways by which ice forms in cirrus clouds is of major climatic relevance (Kärcher, 2017).

1.2 Pathways for atmospheric ice formation

This section introduces the topic of atmospheric ice formation based on a purely phenomenological description of the potential primary ice nucleation modes, as illustrated in Fig. 1.1. A more detailed theoretical description of these processes is given in Chapter 2.

Atmospheric ice nucleation can occur via homogeneous ice nucleation and heterogeneous ice nucleation. Homogeneous ice nucleation is defined as the process by which supercooled water or aqueous solution droplets freeze homogeneously without the need for foreign particles or substrates (Vali et al., 2015). This only occurs at sufficiently low temperatures (typically below about 235 K – the threshold for the spontaneous freezing of pure water droplets), and sufficiently high ambient RHs (needed to achieve a sufficiently high, critical dilution of aqueous solution droplets to enable them to freeze) (Pruppacher et al., 1997). Because such conditions are not always met in the atmosphere, heterogeneous ice nucleation often represents the dominant pathway for primary ice formation. In heterogeneous ice nucleation, certain compositional and surface features of solid aerosol particles catalyze the formation

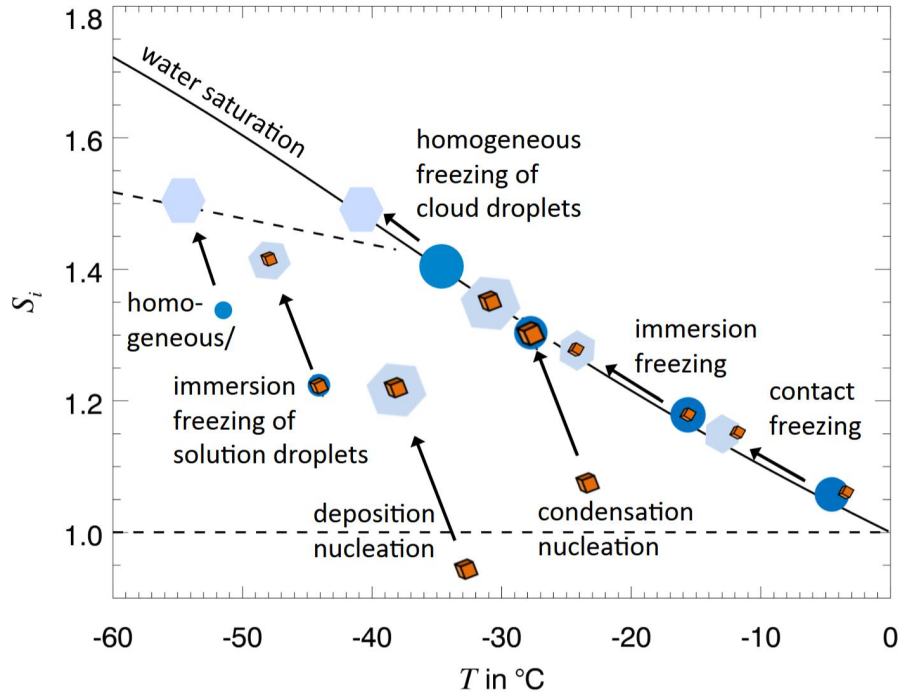


Figure 1.1: Schematic representation of the different ice nucleation modes (taken from Hoose et al. (2012), Fig. 1 therein). The y-axis represents the saturation ratio with respect to ice, later labeled as S_{ice} in this thesis.

of an ice embryo and thereby lower the Gibbs free energy barrier for freezing relative to homogeneous nucleation. Aerosol particles with such features are called INPs, and can initiate ice formation at lower RHs or weaker supercooling than would otherwise be required (Hoose et al., 2012). Their presence, therefore, has a strong influence on the onset of glaciation, cloud phase partitioning, and precipitation formation in cold clouds.

Following Vali et al. (2015), heterogeneous atmospheric ice nucleation can be classified into several modes according to the pathway by which ice first appears.

Deposition nucleation: Deposition nucleation refers to ice nucleation from supersaturated vapor on an INP without prior formation of observable liquid water (Vali et al., 2015). It was historically regarded as an important pathway for cirrus formation and for ice formation on insoluble particles under ice-supersaturated conditions. More recent work, however, has shown that some observations previously attributed to deposition nucleation may instead be explained by **pore condensation and freezing (PCF)**, in which water condenses and subsequently freezes within nanoscale pores. The thermodynamic basis of this mechanism is discussed in subsection 2.1.2.

Immersion freezing: Immersion freezing occurs when an INP is located within a supercooled liquid droplet and initiates freezing from inside the liquid phase (Vali et al., 2015). It is widely regarded as the dominant heterogeneous freezing pathway in mixed-phase clouds.

However, it can also occur under cirrus conditions (see Fig. 1.1: immersion freezing of solution droplets), meaning that immersion of the INP causes the aqueous solution layer to freeze already at a lower dilution (i.e., at a lower ambient RH) than in homogeneous freezing conditions. Consequently, immersion freezing has received extensive experimental and modeling attention (Hoose et al., 2012; Kanji et al., 2017; Knopf et al., 2023; Murray et al., 2012). Parameterizations for immersion freezing are frequently expressed in terms of the ice nucleation active site (INAS) density or related formulations, as described in Chapter 2 (DeMott et al., 2015; Niemand et al., 2012; Ullrich et al., 2017).

Contact freezing: Contact freezing is initiated when an INP triggers freezing at the air-water interface as it contacts a supercooled droplet, or when nucleation occurs at an air-liquid-particle triple interface (Vali et al., 2015). Contact freezing may, in some cases, be more efficient than immersion freezing, but the distinction between the two is experimentally challenging, particularly for atmospheric particles with irregular shapes and complex surface chemistry (Knopf et al., 2023; Vali et al., 2015). For that reason, contact freezing remains less well constrained than immersion freezing in both measurements and models.

Condensation freezing: Condensation freezing is defined by Vali et al. (2015) as freezing initiated concurrently with the initial formation of liquid on a CCN at temperatures below the melting point of ice. Although this pathway has long been discussed conceptually, direct evidence for it as a distinct atmospheric ice nucleation mode remains limited, and its separation from deposition nucleation or immersion freezing is often unclear (Knopf et al., 2023; Vali et al., 2015). In current atmospheric literature, the term is therefore used only rarely and with caution.

1.3 Research on atmospheric ice nucleation: from early studies to current approaches

The study of atmospheric ice nucleation has evolved from phenomenological observations to a multiscale discipline combining molecular theory, targeted laboratory experiments, field observations, and process-resolving as well as climate-scale models. Early work focused on identifying substances capable of initiating freezing and on classifying nucleation modes (Mason et al., 1958; Vonnegut, 1947). Later, the emphasis shifted towards quantifying ice nucleation efficiency and incorporating those data into cloud models (DeMott et al., 2010; Hoose et al., 2012). More recently, the field has moved towards mechanistic explanations that link molecular structure, surface topography, pore geometry, particle composition, and atmospheric aging to the observed freezing behavior (Burrows et al., 2022; Hoose et al., 2012; Knopf et al., 2023; Murray et al., 2012).

At the molecular scale, Classical Nucleation Theory (CNT) has provided an important starting point for interpreting both homogeneous and heterogeneous ice nucleation (detailed later in Chapter 2). CNT offers a thermodynamic framework relating nucleation to the Gibbs free energy cost of forming a critical embryo, but it often relies on idealized assumptions about interfacial energies, substrate geometry, and the identity of the critical nucleus (Knopf et al., 2023; Vali et al., 2015). For atmospheric particles, which are chemically and morphologically complex, these assumptions are often too broad to make accurate predictions.

Molecular Dynamics (MD) simulations have therefore become increasingly important in revealing mechanisms that are inaccessible to bulk experiments. Simulation studies have shown that the ice nucleation ability of a surface does not depend simply on whether it is hydrophilic or hydrophobic, rather it depends on how the surface organizes adjacent water molecules, how well it templates ice-like structures, and whether nanoscale defects promote critical embryo formation (Lupi et al., 2014a; Lupi et al., 2014b; Sosso et al., 2016).

Subsequent work has demonstrated the importance of stacking disorder, polymorph selection, and non-planar geometries such as wedges, pores, and cavities, all of which complicate the classical picture of nucleation on a flat substrate (Bi et al., 2017; Davies et al., 2021; Knopf et al., 2023; Lupi et al., 2017). Recent simulations have also suggested that heterogeneous ice nucleation can be enhanced in water under capillary tension, highlighting the role of mesoscale morphology and confined water in atmospheric particles (Rosky et al., 2023). These advances have shifted the field away from simplified representations of INPs as chemically uniform surfaces and towards a view of nucleation as an emergent property of local structure, molecular ordering, and surface heterogeneity. In this sense, MD studies provide a mechanistic bridge between idealized theory and laboratory observations.

Controlled laboratory experiments remain the core empirical basis of atmospheric ice nucleation research. Reviews by Murray et al. (2012), Hoose et al. (2012), and Kanji et al. (2017), synthesized the rapid increase of droplet-freezing assays, Continuous Flow Diffusion Chamber (CFDC) measurements, and large aerosol/cloud chamber studies. These studies established that different classes of aerosol particles, including mineral dust, biological material, soot, volcanic ash, and marine particles, exhibit widely different ice nucleation efficiencies depending on temperature, RH, particle size, surface chemistry, and phase state (Hoose et al., 2012; Kanji et al., 2017; Murray et al., 2012). Large chamber studies supported the use of the INAS density as a practical metric for comparing materials, particularly for desert dust (Connolly et al., 2009; Niemand et al., 2012; Ullrich et al., 2017). At the same time, direct imaging and spectroscopic work increasingly pointed to the role of discrete active sites rather than uniformly active surfaces (Holden et al., 2019; Holden et al., 2021).

Field studies expanded the scope of the discipline by testing whether laboratory-derived concepts apply to real atmospheric aerosol populations. Measurements of atmospheric INP

concentrations in the boundary layer, free-tropospheric, marine, and continental environments showed that INPs are rare relative to the total number of aerosol particles, spatially variable, and highly sensitive to source regions and transport history (Burrows et al., 2022; DeMott et al., 2010; DeMott et al., 2017). These studies also demonstrated that the abundance of larger aerosol particles and ambient temperature can provide useful first-order constraints on INP concentrations, motivating empirical parameterizations for use in models (DeMott et al., 2010).

Subsequent field campaigns coupled freezing measurements with single-particle composition analyses to identify which aerosol types were actually acting as INPs in different environments (China et al., 2017). These field observations pushed the subject towards source apportionment, atmospheric processing, and environmental variability. In particular, the development of the Portable Ice Nucleation Experiment (PINE) has marked an important advance in atmospheric ice nucleation research, as it enables online measurements of INPs with high temporal resolution and has significantly improved the ability to investigate their occurrence, variability, and atmospheric relevance under field conditions, complementing the existing suite of ice nucleation techniques such as CFDCs and freezing-array methods (Herbert et al., 2026; Möhler et al., 2021). Current understanding suggests that no single descriptor fully captures the atmospheric ice nucleation ability of all particles. Composition matters, but so do crystallographic match, nanoscale roughness, pore structure, organic coatings, phase state, and atmospheric aging. Likewise, no single experimental or theoretical framework is sufficient on its own. Instead, atmospheric ice nucleation is now viewed as a multiscale, probabilistic process governed by the interplay of substrate properties, water activity, temperature, and supersaturation (Knopf et al., 2023; Vali et al., 2015). Overall, the history of atmospheric ice nucleation research reflects the growth of a field that began with descriptive observations of rare freezing events and has developed into a quantitatively rich, interdisciplinary science.

1.4 Atmospheric aging of aerosols

As aerosol particles are transported from the boundary layer to higher altitudes, their surface structure may experience substantial physical, chemical, and morphological modifications depending on temperature, RH, radiation, and the gaseous precursors encountered along their transport pathways. Because ice nucleation is highly sensitive to these surface characteristics, aging processes can profoundly alter the ice nucleation activity of atmospherically relevant aerosol particles (Hoose et al., 2012; Huang et al., 2025; Knopf et al., 2018; Riemer et al., 2019). Although it is sometimes difficult to categorize the complex aging pathways separately, this thesis investigates three important processes, which are defined as follows.

The first pathway can be termed physical mixing or, as used hereafter, **internal mixing**. It describes aging mechanisms through which multiple compositions coexist within a single particle through physical conglomeration (Huang et al., 2025; Riemer et al., 2019). It means that secondary organic material (SOM) and secondary inorganic components like sulfates and nitrates may form on the particle surface of pristine INPs (like freshly mobilized dust particles) after a series of processes including oxidation and condensation, leading to internal mixing. With regard to ice formation under cirrus conditions via the deposition nucleation mode, such condensation of secondary material can partially or completely mask the ice-active sites of the pristine INPs, thereby inhibiting their intrinsic ice nucleation ability. Arguing alternatively in terms of the PCF mechanism, condensation will fill the pores of an INP with potentially viscous organic material, which might not freeze at all, or inorganic aqueous solutes, which have a much lower freezing temperature compared to pure water. For both interpretations, the extent to which the intrinsic ice nucleation ability of an INP is inhibited is dependent on the coating thickness, phase state, viscosity, and the properties of the underlying particle (Knopf et al., 2018; Li et al., 2017; Riemer et al., 2019). At the same time, internal mixing must not necessarily result in a reduction in ice nucleation activity; for example, a newly formed crystalline coating layer might offer on its own active sites for heterogeneous ice formation.

Aerosol particles may also undergo substantial **morphological aging** through cloud processing. During transport through convective or cirrus clouds, particles can be incorporated into cloud droplets or ice crystals and later released as residual particles after evaporation or sublimation. Such processing can alter particle shape, porosity, internal structure, and mixing state, often producing residual particles that differ markedly from freshly emitted aerosols (Adler et al., 2013; Adler et al., 2014). These changes are relevant because surface roughness, pore geometry, and phase separation may all influence heterogeneous ice nucleation pathways. Laboratory studies have shown that cloud processing can significantly modify the ice nucleation ability of aerosol particles, in some cases enhancing their ability to nucleate ice after restructuring during droplet activation, freezing, and drying cycles (Kilchhofer et al., 2021; Mahrt et al., 2020; Wagner et al., 2017; Wagner et al., 2024). Thus, aerosol history within clouds can be an important determinant of subsequent ice formation.

Chemical aging refers to modifications in aerosol composition and surface chemistry caused by condensation, reactive uptake, and heterogeneous reactions involving gaseous precursor species. Oxidized organic vapors and inorganic trace gases can adsorb onto aerosol particles and alter surface functionality, polarity, and reactivity (Knopf et al., 2018; Shiraiwa et al., 2011). In highly viscous or solid particles, mass transport of reactants within the particle bulk may become the rate-limiting step, such that heterogeneous reactions are largely confined to the particle surface (Maria et al., 2004). Hydrogen bonding between oxygenated compounds and functional groups may further promote the formation of amorphous solid or semi-solid

phases (Mikhailov et al., 2009). These chemically induced changes may either enhance or suppress heterogeneous ice nucleation activity by modifying surface functional groups, altering pore structures, changing surface topography, or forming coatings that reduce direct interaction between water vapor and the underlying ice-active substrate. At the same time, oxidation may also remove or restructure organic material that previously masked active sites, thereby exposing mineral or other ice active components and increasing their ice nucleation activity (Jahl et al., 2021).

Collectively, atmospheric aging can substantially modify the ice nucleation potential of aerosol particles and thereby influence cloud microphysical properties in ways that cannot be inferred solely from their primary emission characteristics. Understanding these transformations is therefore essential for linking aerosol sources to their actual climatic impacts. Aged aerosol particles acting as potential seeds for cirrus formation have also been detected in the upper troposphere, where they have been identified through dedicated, though still limited, airborne measurements. This is described in the next section.

1.5 Aerosols relevant to cirrus formation in the upper troposphere

The upper troposphere hosts a chemically diverse and dynamically evolving aerosol population shaped by deep convection, long-range transport, secondary formation, and atmospheric aging. Aerosols reaching these altitudes originate from both natural and anthropogenic sources and often differ substantially from their freshly emitted counterparts. During transport, the particles are exposed to changing temperatures, humidity, radiation, and trace gas environments, which promote condensation, heterogeneous chemistry, cloud processing, and mixing with other aerosol components. As a result, aerosols in the upper troposphere are commonly found as complex internally mixed particles rather than as pristine source-specific species.

A major fraction of the aerosol burden in the upper troposphere consists of inorganic components such as sulfate, nitrate, and ammonium, together with organic material, mineral dust, and black carbon (Appel et al., 2022; Curtius et al., 2024; Ebert et al., 2024; Fadnavis et al., 2013; Gu et al., 2016; Höpfner et al., 2019; Neely III et al., 2014; Lau et al., 2018; Lelieveld et al., 2018; Vernier et al., 2011; Weigel et al., 2021; Xenofontos et al., 2024; Yu et al., 2015). Among these, sulfate plays a particularly important role in atmospheric aerosol composition because sulfuric acid is readily formed through oxidation of sulfur dioxide and condenses efficiently under most atmospheric conditions. Sulfate-containing particles frequently serve as cores for further condensational growth and multi-phase chemical processing. Ammonia and nitric acid can partition into these particles, leading to the formation of mixed inorganic aerosol populations whose composition depends strongly on temperature, RH, and particle acidity (Karydis et al., 2021; Martin et al., 2003; Meng et al., 2020; Nenes

et al., 2020). Consequently, upper tropospheric aerosols often contain variable mixtures of sulfate, nitrate, and ammonium, reflecting both precursor availability and the thermodynamic conditions encountered during transport.

Organic aerosol constitutes another major component of the upper tropospheric aerosol population. It originates from both primary emissions and the oxidation of VOCs from biogenic and anthropogenic sources. In particular, isoprene and other hydrocarbons can contribute substantially to SOA formation after oxidation and condensational growth (Andreae et al., 2015; Curtius et al., 2024; Fu et al., 2016; Goldstein et al., 2007; Mishra et al., 2020; Palmer et al., 2006; Palmer et al., 2022; Shen et al., 2024b; Zha et al., 2023). Organic material in the upper troposphere may occur in liquid, semi-solid, or glassy states, depending on environmental conditions and chemical composition, and this phase behavior strongly influences particle reactivity, mixing state, and cloud-forming ability. Because organics are frequently mixed with sulfate and other inorganic species, they contribute substantially to the chemical and microphysical complexity of upper tropospheric aerosols.

In addition to secondary inorganic and organic aerosol components, primary particles such as mineral dust and black carbon are also transported efficiently to the upper troposphere. Once lofted, these particles may act as substrates for condensation and heterogeneous chemistry, thereby becoming incorporated into internally mixed aerosol populations (Clarke et al., 2004; Deboudt et al., 2010; Froyd et al., 2009; Sullivan et al., 2007). Their physicochemical properties can therefore evolve substantially during transport, which in turn influences their radiative effects and their interactions with clouds. Deep convective transport is particularly important in this context, as it can rapidly inject boundary-layer air masses, precursor gases, and particles into the upper troposphere, where subsequent processing can modify aerosol composition on relatively short timescales (Wang et al., 2000; Yin et al., 2012).

Overall, the chemical composition of aerosol particles in the upper troposphere reflects the combined influences of source emissions, secondary formation, gas-particle partitioning, and atmospheric aging. This complexity is especially relevant for aerosol-cloud interactions, because particle composition, phase state, and mixing state all influence the ability of aerosol particles to act as INPs.

1.6 Thesis outline

This thesis investigates how atmospheric aging modifies the ice nucleation ability of aerosol particles under cirrus cloud conditions. It is organized around three major research themes, each addressing a distinct pathway of aerosol aging and its implications for the particles' ice nucleation activity: (i) aging by internal mixing through condensation of secondary organic and inorganic material, (ii) morphological aging by ice cloud processing, and (iii)

chemical aging through reactive uptake of organic precursors. The aerosol systems under investigation are members of the complex family of particles that are generally present in the upper troposphere, as outlined in the preceding section.

Each of the three research themes is presented in a separate chapter (Chapter 4, Chapter 5, and Chapter 6). Each chapter provides another detailed introduction to the specific scientific background of the investigated aerosol system and outlines the motivation for carrying out the particular aging experiments. Here, these topics are therefore only briefly summarized: Chapter 4 deals with the internal mixing of mineral dust particles with a large variety of secondary materials, including sulfate, nitrate, ammonium, and organics. Chapter 5 investigates the morphological aging of isoprene-derived SOA particles during processing in deep-convective and cirrus clouds. The third research theme, presented in Chapter 6, investigates chemical aging through multi-phase reactions and reactive uptake of organic precursor gases (glyoxal and isoprene) on sulfuric acid and ammonium sulfate seed particles.

The research approach is experimental in nature and uses two large-scale laboratory setups, respectively, cloud chambers, to realistically simulate atmospheric aging pathways at low temperatures. These are the Aerosol Interaction and Dynamics in the Atmosphere (AIDA) facility at the Karlsruhe Institute of Technology (KIT) and the Cosmics Leaving Outdoor Droplets (CLOUD) experiment at the European Organization for Nuclear Research (CERN). Both facilities offer ideal conditions for conducting aging experiments over long timescales, and both have advanced instrumentation for detecting, e.g., the morphological and chemical changes in processed aerosol particles. The cloud chambers were used as “reaction tanks” to process the particles, while their ice nucleation activity was measured continuously during aging with two types of CFDCs. These laboratory experiments offer the advantage of isolating specific processes and examining them in well-controlled thermodynamic and chemical environments, thereby helping to interpret field measurements that capture aerosol properties in authentic but highly variable atmospheric conditions.

Before turning to the results chapters, Chapter 2 provides an introduction to the theoretical concepts for describing ice nucleation, while the experimental facilities, measurement techniques, and instrumentation employed throughout this work are described in Chapter 3. Following the results chapters, Chapter 7 synthesizes the principal findings of this thesis and discusses their broader atmospheric implications.

2 Theoretical background

This chapter introduces the theoretical concepts that form the basis of the studies discussed in this thesis. The chapter begins by describing nucleation as a fundamental phase transition process involved in atmospheric aerosol and cloud formation. The discussion then shifts to atmospheric ice nucleation and its role in the formation of cirrus clouds. Here, it will be explained how the ice nucleation activity is quantified and parameterized in laboratory studies, field observations, and atmospheric models.

2.1 Nucleation

Atmospheric aerosols can form directly in the atmosphere when precursor gases nucleate to form new particles. Nucleation is a phase transition process in which molecules or molecular clusters of a new phase become stable enough to continue growing. This requires forming a small cluster of the new phase and overcoming the Gibbs free energy barrier, which is defined as the thermodynamic potential of a system at constant pressure and temperature. A transformation from an initial phase A to a new phase B, therefore, begins with the formation of a small cluster of phase B within phase A. If this cluster becomes larger than a critical size, further growth becomes thermodynamically favorable, and the phase transformation proceeds. Nucleation theory aims to describe the rate at which such stable clusters, or nuclei, are formed.

Nucleation can occur with or without the help of a foreign surface. In homogeneous nucleation, the new phase spontaneously forms within the parent phase. In heterogeneous nucleation, the new phase forms on a pre-existing surface, such as an aerosol particle. Such surfaces can lower the Gibbs free energy barrier for the formation of the new phase. As a result, heterogeneous nucleation generally occurs at supersaturations lower than those required for homogeneous nucleation (Pruppacher et al., 1997; Seinfeld et al., 2012).

2.1.1 Homogeneous nucleation

Homogeneous nucleation describes the formation of a new stable condensed phase from a supersaturated parent phase in the absence of foreign surfaces, pre-existing particles, or other heterogeneous nucleation sites. In the case of vapor-to-liquid nucleation, small molecular clusters form continuously through random molecular collisions. Most of these clusters are

unstable and evaporate again, but under sufficiently supersaturated conditions, some clusters may grow large enough to become stable nuclei.

For a condensable species A in air at temperature T , the saturation ratio is defined as

$$S = \frac{p_A}{p_A^s(T)}, \quad (2.1)$$

where p_A is the partial pressure of species A , and $p_A^s(T)$ is the saturation vapor pressure over a flat surface of the condensed phase. Supersaturation corresponds to $S > 1$, and provides the thermodynamic driving force for nucleation.

For an ideal vapor, the chemical potential difference between the vapor and condensed phases is

$$\Delta\mu = \mu_v - \mu_c = k_B T \ln S, \quad (2.2)$$

where μ_v and μ_c are the chemical potentials of the vapor and condensed phases, respectively, and k_B is the Boltzmann constant. Under supersaturated conditions, $S > 1$, so $\Delta\mu > 0$, meaning that transfer of molecules from the vapor to the condensed phase is thermodynamically favorable.

In Classical Nucleation Theory (CNT), the change in Gibbs free energy associated with forming a spherical condensed cluster of radius r is written as the sum of two related terms: a positive surface free energy term and a negative volume free energy term. The surface term accounts for the energetic cost of creating a new vapor-liquid interface,

$$\Delta G_{\text{surface}} = 4\pi r^2 \sigma, \quad (2.3)$$

where σ is the interfacial tension between the condensed phase and the surrounding vapor. The volume term represents the thermodynamic gain from transferring molecules from the supersaturated vapor phase into the more stable condensed phase.

$$\Delta G_{\text{volume}} = -\frac{4}{3}\pi r^3 \frac{\Delta\mu}{v_m}, \quad (2.4)$$

where v_m is the molecular volume of the condensed phase. The total Gibbs free energy change is therefore

$$\Delta G(r) = 4\pi r^2 \sigma - \frac{4}{3}\pi r^3 \frac{\Delta\mu}{v_m}. \quad (2.5)$$

At a small radius, the surface term dominates, and the nucleus formation is unfavorable. At a larger radius, the volume term becomes dominant, and the growth becomes favorable to form a critical nucleus. This relation produces a maximum in $\Delta G(r)$, corresponding to the critical nucleus.

The critical radius, denoted here as r^* , is obtained by setting

$$\frac{d\Delta G}{dr} = 0. \quad (2.6)$$

Using Eq. (2.5), this gives

$$r^* = \frac{2\sigma v_m}{\Delta\mu} = \frac{2\sigma v_m}{k_B T \ln S}. \quad (2.7)$$

Thus, the critical radius decreases as the saturation ratio increases. Higher supersaturation, therefore, makes it possible for smaller clusters to become stable nuclei. The Gibbs free energy barrier for homogeneous nucleation is obtained by evaluating $\Delta G(r)$ at $r = r^*$:

$$\Delta G^* = \Delta G(r^*) = \frac{16\pi}{3} \frac{\sigma^3 v_m^2}{(k_B T \ln S)^2}. \quad (2.8)$$

This expression shows that the nucleation barrier decreases strongly with increasing supersaturation. Since $\Delta G^* \propto (\ln S)^{-2}$, even a modest increase in S can significantly lower the Gibbs free energy barrier and enhance the probability of forming stable nuclei.

The critical radius distinguishes between unstable clusters and stable growing clusters that result in nucleation. For $r < r^*$, the cluster is subcritical. In this regime, the Gibbs free energy increases with increasing radius, so growth is thermodynamically unfavorable and evaporation is favored. Such clusters are more likely to lose molecules than to grow. For $r = r^*$, the cluster is at the top of the Gibbs free energy barrier. This state corresponds to an unstable equilibrium. A critical cluster has an approximately equal probability of growing or shrinking: if it gains molecules, it becomes supercritical, and growth becomes favorable; if it loses molecules, it becomes subcritical and tends to evaporate. For $r > r^*$, the cluster is supercritical. In this regime, the Gibbs free energy decreases with increasing radius, so further growth lowers the Gibbs free energy of the system. The cluster is therefore thermodynamically favored to grow spontaneously if sufficient vapor is available.

The same condition can be interpreted using the Kelvin equation, which describes the equilibrium vapor pressure over a curved liquid surface. For a spherical droplet,

$$\ln S = \frac{2\sigma v_m}{r k_B T}. \quad (2.9)$$

Rearranging this expression gives

$$r = \frac{2\sigma v_m}{k_B T \ln S}, \quad (2.10)$$

which is identical to the critical radius obtained from the Gibbs free energy criterion. Therefore, the critical cluster may also be viewed as a droplet in unstable equilibrium with the surrounding supersaturated vapor. If $r < r^*$, the equilibrium vapor pressure over the

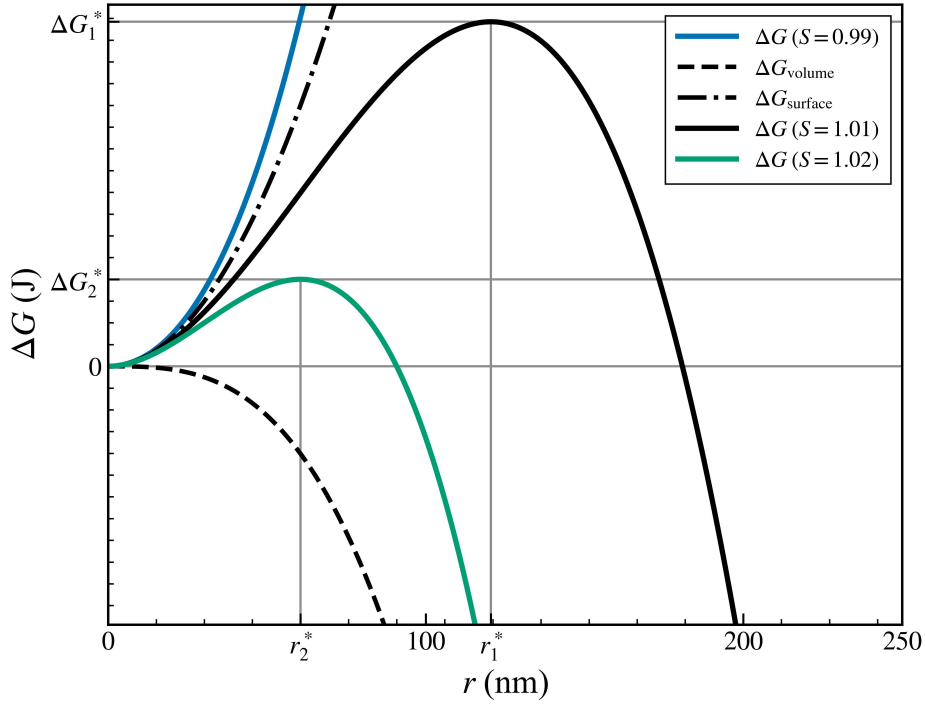


Figure 2.1: Variation of the Gibbs free energy change as a function of the droplet radius at a temperature of 273.15 K, assuming $\sigma = 0.072 \text{ J m}^{-2}$ and $v_m = 3 \times 10^{-29} \text{ m}^3/\text{molecule}$, for three saturation ratios: $S = 0.99$, $S = 1.01$, and $S = 1.02$. The volume free energy contribution and surface free energy contribution are shown for $S = 1.01$. The quantities ΔG_1^* and ΔG_2^* indicate Gibbs free energy barriers at the corresponding radii r_1^* and r_2^* .

curved cluster surface is greater than the ambient vapor pressure, and evaporation is favored. If $r > r^*$, the ambient vapor pressure is greater than the equilibrium vapor pressure over the curved surface, and condensation is favored.

The homogeneous nucleation rate, J_{hom} , is commonly expressed in CNT as

$$J_{\text{hom}} = Z \beta^* N^*, \quad (2.11)$$

where Z is the Zeldovich factor, β^* is the molecular attachment rate to a critical cluster, and N^* is the equilibrium number concentration of critical clusters (Pruppacher et al., 1997). The Zeldovich factor corrects for the fact that not every cluster that reaches the critical size (critical nucleus) will continue to grow, but some might shrink back. The concentration of critical clusters is commonly written using a Boltzmann factor,

$$N^* = N_1 \exp\left(-\frac{\Delta G^*}{k_B T}\right), \quad (2.12)$$

where N_1 is the monomer number concentration. Substituting this into Eq. (2.11) gives

$$J_{\text{hom}} = Z \beta^* N_1 \exp\left(-\frac{\Delta G^*}{k_B T}\right). \quad (2.13)$$

This expression shows that the nucleation rate depends exponentially on the Gibbs free energy change. Since ΔG^* decreases rapidly as supersaturation increases, the nucleation rate is extremely sensitive to S . This is illustrated in Fig. 2.1. At low supersaturation ($S = 1.01$, black line), ΔG^* is large, and the exponential term is very small, so nucleation is rare. At high supersaturation ($S = 1.02$, green line), ΔG^* becomes smaller, the population of critical clusters increases, and the nucleation rate can rise by many orders of magnitude. For vapor-to-liquid nucleation, the molecular attachment rate to a critical cluster may be approximated as

$$\beta^* = 4\pi(r^*)^2 \alpha \frac{p_A}{\sqrt{2\pi m k_B T}}, \quad (2.14)$$

where α is the mass accommodation coefficient and m is the molecular mass of the condensing species. The factor $4\pi(r^*)^2$ represents the surface area of the critical cluster, while the remaining term represents the molecular flux from the vapor phase to the cluster surface.

A central assumption in CNT is the capillary approximation. In this approximation, a molecular cluster containing only a small number of molecules is treated as if it were a macroscopic spherical liquid droplet. Therefore, the cluster is assigned bulk liquid properties, including the bulk liquid density, molecular volume, and planar surface tension. This approximation makes the theory mathematically simple and allows the nucleation barrier, critical radius, and nucleation rate to be written in closed-form. However, it is also one of the major limitations of CNT (Seinfeld et al., 2012).

Because the nucleation rate depends exponentially on ΔG^* , even small errors in the estimated surface tension or cluster free energy can produce very large errors in the predicted nucleation rate. CNT may therefore provide a useful qualitative framework and may predict trends with temperature and supersaturation, but it often fails to reproduce the absolute magnitude of experimentally measured nucleation rates.

2.1.2 Heterogeneous nucleation

Heterogeneous nucleation occurs when a foreign surface helps the new phase to form. In the atmosphere, these surfaces are usually aerosol particles. Compared with homogeneous nucleation, heterogeneous nucleation lowers the Gibbs free energy barrier and therefore allows nucleation to occur at lower supersaturation conditions.

In CNT, the Gibbs free energy of formation of a critical cluster on a flat, insoluble solid surface (see Fig. 2.2) is written as

$$\Delta G_{\text{het}}^* = \Delta G_{\text{hom}}^* f(m), \quad (2.15)$$

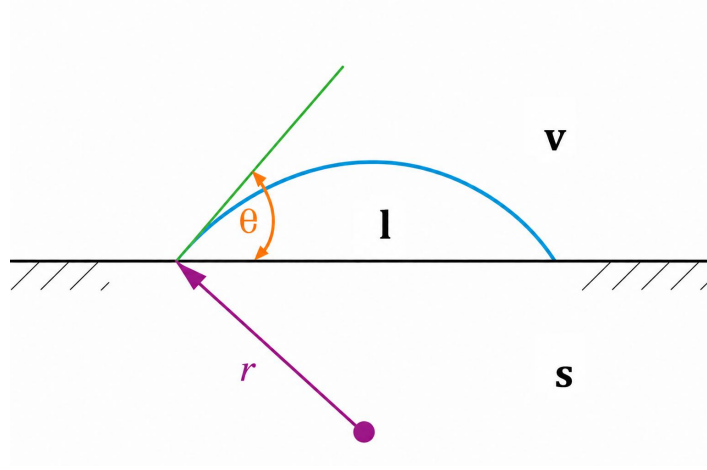


Figure 2.2: Schematic representation of cluster formation on an insoluble flat surface. The angle θ is the contact angle between the cluster and the substrate. Adapted from Seinfeld et al. (2012).

where ΔG_{hom}^* is the homogeneous nucleation barrier and $f(m)$ is a geometric factor that describes how strongly the surface reduces this barrier. The factor depends on the contact parameter m , defined as

$$m = \cos \theta = \frac{\sigma_{\text{sv}} - \sigma_{\text{sl}}}{\sigma_{\text{lv}}}, \quad (2.16)$$

where θ is the contact angle between the critical cluster and the substrate. The terms σ_{sv} , σ_{sl} , and σ_{lv} are the solid-vapor, solid-liquid, and liquid-vapor interfacial tensions, respectively. In the context of ice nucleation, the liquid phase in this notation may represent an ice cluster, depending on the process considered.

For a spherical-cap cluster on a flat surface, the geometric factor is

$$f(m) = \frac{1}{4}(2 + m)(1 - m)^2. \quad (2.17)$$

The function $f(m)$ is the geometric correction factor that accounts for the reduction in the nucleation energy barrier caused by the presence of a surface. It varies between 0 and 1 for contact angles in the range $0^\circ \leq \theta \leq 180^\circ$, where $m = \cos \theta$. When $\theta = 0^\circ$, $m = 1$, and $f(m) = 0$. This represents complete wetting, in which the surface fully supports the formation of the condensed phase, and the heterogeneous nucleation barrier vanishes. In contrast, when $\theta = 180^\circ$, $m = -1$, and $f(m) = 1$; hence, the barrier is the same as that for homogeneous nucleation. Thus, smaller contact angles indicate more efficient nucleating surfaces, as shown in Fig. 2.3.

This treatment assumes a flat substrate surface. Atmospheric aerosol particles, however, are curved. Surface curvature can modify the Gibbs free energy barrier. Fletcher (1958)

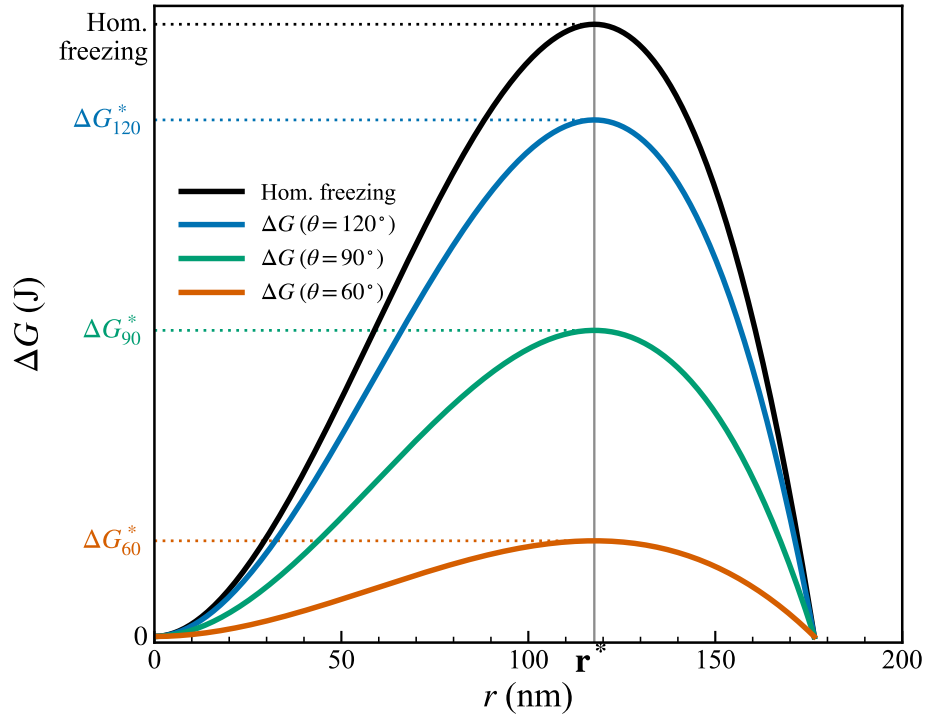


Figure 2.3: Variation of the Gibbs free energy change as a function of nucleus radius for heterogeneous nucleation on a solid surface at fixed temperature of 273.15 K, assuming $\sigma = 0.072 \text{ J m}^{-2}$ and $v_m = 3 \times 10^{-29} \text{ m}^3/\text{molecule}$, for different contact angles of 60° , 90° , and 120° . The reduction of the heterogeneous Gibbs free energy barrier relative to homogeneous nucleation is indicated schematically.

considered heterogeneous nucleation on a spherical substrate and expressed the heterogeneous nucleation barrier as

$$\Delta G_{\text{het}}^* = \Delta G_{\text{hom}}^* f(m, x) = \frac{16\pi}{3} \frac{v_l^2 \sigma_{lv}^3}{(k_B T \ln S)^2} f(m, x), \quad (2.18)$$

where v_l is the molecular volume of the nucleating phase, σ_{lv} is the interfacial tension between the cluster and the surrounding phase, and x is the ratio between the substrate radius (R) and the critical cluster radius (r^*),

$$x = \frac{R}{r^*}. \quad (2.19)$$

The critical cluster radius is given by

$$r^* = \frac{2v_l \sigma_{lv}}{k_B T \ln S}. \quad (2.20)$$

The geometric correction factor $f(m, x)$ in Equation 2.18 accounts for both the curvature of the substrate and the geometry of the cluster. The contact angle is therefore a key parameter in heterogeneous nucleation theory.

McDonald (1964) estimated a relationship between contact angle and critical supersaturation for the droplet formation on insoluble particles. For cloud droplet formation at ambient supersaturations below a few percent, only particles with sufficiently small contact angles can act as effective nuclei.

Representing the interaction between a nucleating cluster and a substrate by a single macroscopic contact angle is a simplification. CNT usually assumes a smooth, chemically uniform, insoluble surface. It neglects microscopic roughness, lattice structure, chemical heterogeneity, pores, defects, and surface diffusion of adsorbed molecules. These properties can strongly influence heterogeneous nucleation in real atmospheric particles. Despite these limitations, CNT remains useful because it explains how surfaces reduce nucleation barriers and provides a basis for more empirical or semi-empirical ice nucleation parameterizations (Fletcher, 1958; Pruppacher et al., 1997; Seinfeld et al., 2012).

2.2 Atmospheric ice nucleation

2.2.1 General considerations

Application of nucleation theory to atmospheric ice formation requires consideration of the thermodynamic properties of water and the aerosol particles that provide potential nucleation sites. The exchange of water between condensed and vapor phase is fundamental for cloud formation. At thermodynamic equilibrium, the molecular flux from a condensed phase to the vapor is balanced by the opposing flux from the vapor to the condensed phase. The corresponding water-vapor partial pressure is the saturation vapor pressure, which depends strongly on temperature and on whether the vapor is in equilibrium with liquid water or ice.

For equilibrium between a condensed phase and its vapor, the rate of change of saturation vapor pressure with temperature is determined by the latent heat of the phase transition, the absolute temperature, and the difference between the specific volumes of the vapor and condensed phases. Because the specific volume of water vapor is much larger than that of liquid water or ice, the contribution of the condensed phase can usually be neglected. If the water vapor is also assumed to behave as an ideal gas, the equation reduces to the Clausius-Clapeyron relation. For equilibrium with ice,

$$\frac{d \ln p_{\text{sat,ice}}(T)}{dT} = \frac{L_s(T)}{R_v T^2}, \quad (2.21)$$

where $p_{\text{sat,ice}}(T)$ is the saturation vapor pressure over ice, $L_s(T)$ is the latent heat of sublimation, and R_v is the gas constant for water vapor. According to this relation, the rate of change of the natural logarithm of saturation vapor pressure with temperature is proportional to the latent heat of phase change and inversely proportional to the square of the absolute temperature.

The resulting expression shows that saturation vapor pressure increases exponentially with temperature. The relevant latent heat, and therefore the saturation vapor pressure, depends on whether the condensed phase is liquid water or ice. For equilibrium over a liquid-water surface, the phase transition is vaporization, and the appropriate quantity is the latent heat of vaporization. The corresponding saturation vapor pressure is commonly referred to as the saturation vapor pressure over water. For equilibrium over an ice surface as shown in Eq. (2.21), the transition is sublimation, and the relevant quantity is the latent heat of sublimation. This gives the saturation vapor pressure over ice.

The latent heat of sublimation is equal to the sum of the latent heat of vaporization and the latent heat of fusion. It is therefore larger than the latent heat of vaporization. As a result, the temperature dependence of saturation vapor pressure over ice differs from that over liquid water. The two saturation vapor pressures are equal at the triple-point temperature, where ice, liquid water, and water vapor can coexist in thermodynamic equilibrium. Below this temperature, however, the saturation vapor pressure over ice is lower than the saturation vapor pressure over liquid water.

Carefully reviewed parameterizations for the temperature-dependent saturation vapor pressures over supercooled liquid water ($p_{\text{sat,liq}}$) and over ice ($p_{\text{sat,ice}}$) were presented by Murphy et al. (2005) (Fig. 2.4, panel a). Due to the fact that $p_{\text{sat,liq}}$ is higher than $p_{\text{sat,ice}}$ below the melting point, air that is saturated with respect to liquid water is supersaturated with respect to ice. This can be expressed by evaluating the ice saturation ratio under water-saturated conditions. Since $p_v = p_{\text{sat,liq}}$ for air saturated with respect to liquid water,

$$S_{\text{ice}} = \frac{p_{\text{sat,liq}}}{p_{\text{sat,ice}}}. \quad (2.22)$$

This quantity represents the ice saturation ratio corresponding to water-saturated air and is shown as a function of temperature (T) in panel (b) of Fig. 2.4.

The difference between saturation vapor pressure over liquid water and over ice increases as temperature decreases below the melting point, reaching a maximum near 262 K (see panel (c) of Fig. 2.4). This distinction is important for cloud microphysics because air can be subsaturated with respect to liquid water while remaining supersaturated with respect to ice. Under such conditions, ice crystals can form and grow even when liquid water droplets are not thermodynamically stable. This provides the thermodynamic basis for ice growth from vapor and for cirrus-relevant heterogeneous ice nucleation pathways, including deposition nucleation and pore condensation and freezing (PCF).

The saturation ratio with respect to ice, (S_{ice}), under water-subsaturated conditions, is defined as

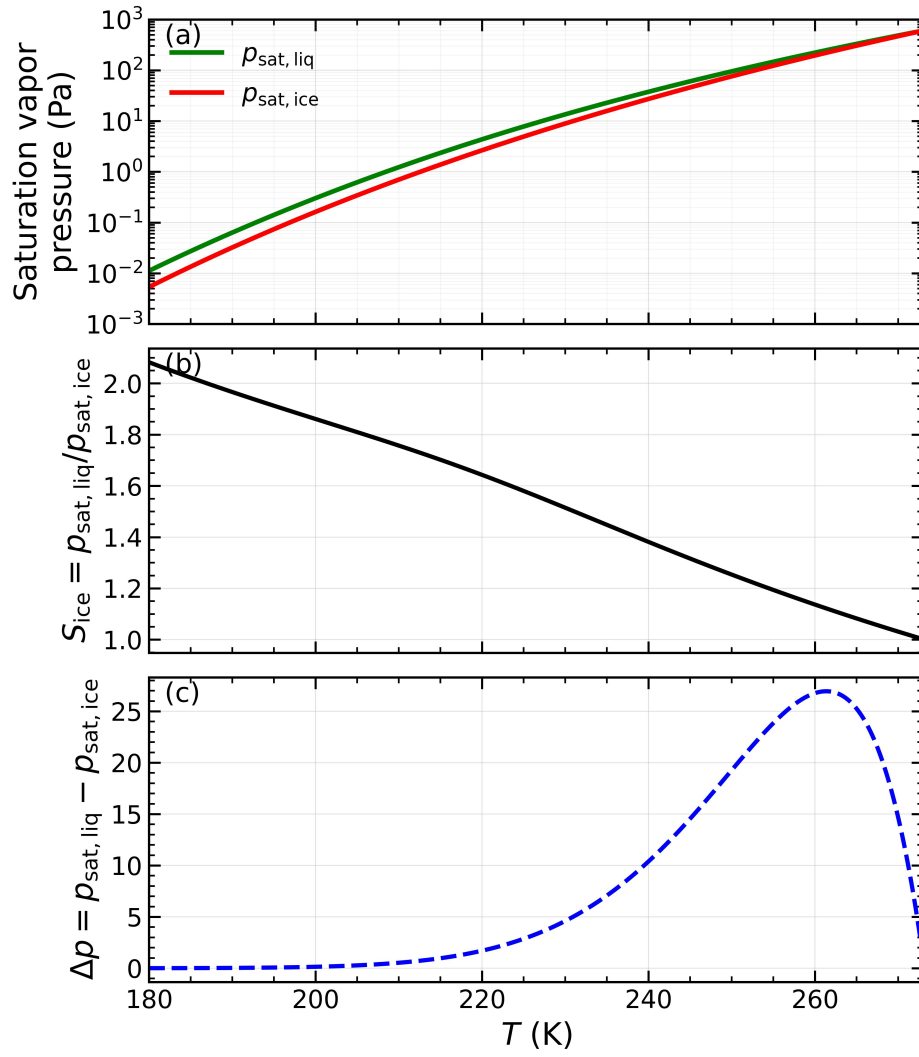


Figure 2.4: Temperature dependence of saturation vapor pressure calculated following Murphy et al. (2005). (a) Saturation vapor pressure over supercooled liquid water, ($p_{\text{sat,liq}}$) (green line), and over ice, ($p_{\text{sat,ice}}$) (red line). (b) Ice saturation ratio under water-saturated conditions, ($S_{\text{ice}} = p_{\text{sat,liq}}/p_{\text{sat,ice}}$). (c) Difference between the saturation vapor pressures, ($\Delta p = p_{\text{sat,liq}} - p_{\text{sat,ice}}$), which reaches a maximum near 262 K.

$$S_{\text{ice}} = \frac{p_v}{p_{\text{sat,ice}}(T)}, \quad (2.23)$$

where p_v is the ambient water vapor partial pressure and $p_{\text{sat,ice}}(T)$ is the saturation vapor pressure over ice at temperature T . Ice supersaturation occurs when $S_{\text{ice}} > 1$. Under these conditions, ice nucleation can occur if the temperature and ice supersaturation are sufficient for an ice embryo to exceed the critical radius. Embryos larger than this critical radius are thermodynamically stable with respect to further growth and can develop into ice crystals.

2.2.2 Cirrus cloud formation

Cirrus clouds form through homogeneous freezing of supercooled aqueous solution droplets or via heterogeneous ice nucleation on pre-existing aerosol particles (Hoose et al., 2012; Murray et al., 2012; Vali et al., 2015, see the phenomenological description in Section 1.2). Homogeneous ice nucleation occurs when ice forms spontaneously within supercooled solution droplets. It requires high ice supersaturation and is mainly relevant at temperatures below approximately 235 K (Koop et al., 2000; Pruppacher et al., 1997). Because homogeneous freezing can produce large numbers of small ice crystals over short timescales, it is an important pathway for cirrus formation and can strongly affect cirrus radiative properties.

A widely used formulation of homogeneous freezing is based on the water-activity criterion of Koop et al. (2000). This framework shows that homogeneous ice nucleation in aqueous solution droplets depends primarily on the water activity of the solution rather than on the specific chemical identity of the solute. The homogeneous ice nucleation rate coefficient is expressed as

$$\log J_{\text{hom}} = -906.7 + 8502 \Delta a_w - 26924 (\Delta a_w)^2 + 29180 (\Delta a_w)^3, \quad (2.24)$$

where J_{hom} is given in $\text{cm}^{-3} \text{s}^{-1}$, and

$$\Delta a_w(T) = a_w(T) - a_w^i(T). \quad (2.25)$$

Here, $a_w(T)$ is the water activity of the aqueous solution droplet, and $a_w^i(T)$ is the water activity of a solution in equilibrium with ice at temperature T . The latter can be written as

$$a_w^i(T) = \frac{p_{\text{sat,ice}}(T)}{p_{\text{sat,liq}}(T)}, \quad (2.26)$$

where $p_{\text{sat,ice}}(T)$ is the saturation vapor pressure over ice and $p_{\text{sat,liq}}(T)$ is the saturation vapor pressure over supercooled liquid water (see Fig. 2.4). This approach provides a general basis for predicting homogeneous freezing thresholds in aqueous solution droplets.

Heterogeneous ice nucleation is initiated by ice-nucleating particles (INPs), which lower the Gibbs free energy barrier for the formation of a critical ice embryo. Because heterogeneous ice nucleation can occur at lower ice supersaturations and higher temperatures than homogeneous freezing, its importance depends on temperature, ice supersaturation, cooling rate, and the abundance, composition, size, surface area, and mixing state of INPs (Hoose et al., 2012; Knopf et al., 2023; Murray et al., 2012; Vali et al., 2015). Parameterizations of heterogeneous ice nucleation differ in how they represent the freezing process. Two limiting descriptions are commonly used: the singular, or deterministic approach, and the stochastic approach (Vali, 2014; Vali et al., 2015). In the singular approach, each particle is assumed to contain active sites with characteristic activation temperatures. Freezing occurs when the temperature falls

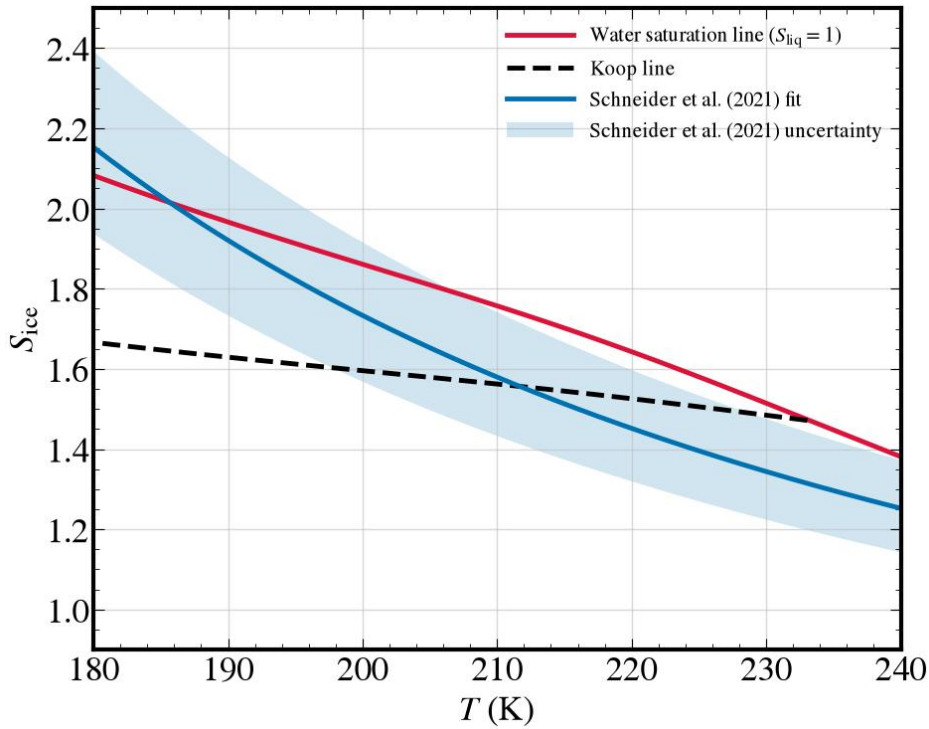


Figure 2.5: Schematic representation of the temperature-dependent ice saturation ratio, S_{ice} , at which homogeneous freezing of aqueous solute particles typically occurs in atmospheric aerosols. The red curve denotes liquid-water saturation. The dashed black line indicates an approximate homogeneous freezing threshold based on the water-activity criterion of Koop et al. (2000). The blue curve shows the Schneider et al. (2021) parameterization derived from AIDA expansion experiments with sulfuric acid solution droplets; the shaded region denotes the uncertainty range associated with that fit.

below the activation temperature of the most efficient active site on the particle. In this view, the frozen fraction depends mainly on temperature and on the distribution of active sites among the aerosol population, while time dependence is not represented explicitly. In contrast, the stochastic approach treats freezing as a time-dependent process, in which the probability of ice formation increases with exposure time under given thermodynamic conditions.

Fig. 2.5 shows thermodynamic reference curves based on parameterizations from previous measurements. The homogeneous freezing threshold based on the water-activity criterion formulated by Koop et al. (2000) (as discussed above) is represented by the dashed black line in the figure. Ice nucleation measurements below this threshold are usually interpreted as heterogeneous ice nucleation, whereas measurements at or above this threshold may be consistent with homogeneous freezing. The blue solid line represents the homogeneous freezing parameterization of Schneider et al. (2021), which was derived from Aerosol Interaction and Dynamics in the Atmosphere (AIDA) cloud chamber expansion experiments with sulfuric acid solution droplets at lower temperatures. Compared with the parameterization

of Koop et al. (2000), Schneider et al. (2021) found higher ice onset values for homogeneous ice nucleation of sulfuric acid solution droplets at lower temperatures between 185 K and 205 K. The red line indicates water saturation, $S_{\text{liq}} = 1$, and defines the conditions at which air is saturated with respect to liquid water. Together, these curves provide a useful reference for distinguishing ice nucleation pathways under cirrus-relevant conditions.

Laboratory experiments and field observations are used to quantify the ice nucleation activity of aerosols over a wide range of temperatures and supersaturations. Important laboratory methods include cloud chamber expansion experiments, Continuous Flow Diffusion Chambers (CFDCs), and droplet freezing assays. In these experiments, ice nucleation activity is often quantified by normalizing the number concentration of ice crystals formed to the number concentration of aerosol particles exposed to the relevant thermodynamic conditions. This ratio is referred to as the activated fraction (AF). The AF is defined as

$$\text{AF} = \frac{N_{\text{ice}}}{N_{\text{aer}}}, \quad (2.27)$$

where N_{ice} is the number concentration of ice crystals formed and N_{aer} is the number concentration of aerosol particles exposed to the relevant thermodynamic conditions.

Another commonly used measure is the ice nucleation active site (INAS) density, which normalizes ice nucleation activity by the aerosol surface area available for ice formation. The INAS density, n_s , relates ice nucleation efficiency to the aerosol surface area available for the formation of a critical ice embryo. It is based on the concept that ice nucleation occurs at discrete active sites on particle surfaces and that the expected number of active sites increases with particle surface area (Connolly et al., 2009; Hoose et al., 2012; Murray et al., 2012; Niemand et al., 2012). For monodisperse particles with surface area A , the activated fraction can be written as

$$\text{AF}(T, S_{\text{ice}}) = 1 - \exp(-n_s(T, S_{\text{ice}})A), \quad (2.28)$$

where $\text{AF}(T, S_{\text{ice}})$ is the fraction of particles that have nucleated ice at temperature T and ice saturation ratio S_{ice} . Rearranging Eq. (2.28) gives

$$n_s(T, S_{\text{ice}}) = -\frac{\ln(1 - \text{AF}(T, S_{\text{ice}}))}{A}. \quad (2.29)$$

For a size-distributed aerosol population, the total aerosol number concentration is

$$N_{\text{aer}} = \sum_i N_{\text{aer},i}, \quad (2.30)$$

where $N_{\text{aer},i}$ is the aerosol number concentration in size bin i . Applying the surface-site formulation to each size bin gives

$$N_{\text{ice},i}(T, S_{\text{ice}}) = N_{\text{aer},i} (1 - \exp(-n_s(T, S_{\text{ice}})A_i)), \quad (2.31)$$

where A_i is the surface area of one particle in size bin i . The total number concentration of ice crystals formed is then obtained by summing over all size bins:

$$N_{\text{ice}}(T, S_{\text{ice}}) = \sum_i N_{\text{aer},i} (1 - \exp(-n_s(T, S_{\text{ice}})A_i)). \quad (2.32)$$

The corresponding activated fraction of the full aerosol population is therefore

$$\text{AF}(T, S_{\text{ice}}) = \frac{N_{\text{ice}}(T, S_{\text{ice}})}{N_{\text{aer}}} = \frac{1}{N_{\text{aer}}} \sum_i N_{\text{aer},i} (1 - \exp(-n_s(T, S_{\text{ice}})A_i)). \quad (2.33)$$

For small frozen fractions, where $n_s(T)A_i \ll 1$ for all size bins, the exponential term can be linearized:

$$1 - \exp(-n_s(T, S_{\text{ice}})A_i) \approx n_s(T, S_{\text{ice}})A_i. \quad (2.34)$$

Substituting this approximation into Eq. (2.32) yields

$$N_{\text{ice}}(T, S_{\text{ice}}) \approx n_s(T, S_{\text{ice}}) \sum_i N_{\text{aer},i} A_i. \quad (2.35)$$

The total aerosol surface area concentration is

$$A_{\text{tot}} = \sum_i N_{\text{aer},i} A_i. \quad (2.36)$$

Thus, in the small-frozen-fraction limit, the INAS density can be obtained directly from the ratio of the ice crystal number concentration to the total aerosol surface area concentration:

$$n_s(T, S_{\text{ice}}) \approx \frac{N_{\text{ice}}}{A_{\text{tot}}}. \quad (2.37)$$

The INAS-density approach therefore provides a surface-area-normalized measure of ice nucleation ability, making it useful for comparing different aerosol samples and experimental conditions. It has been widely applied to immersion freezing, particularly for mineral dust particles. However, n_s is usually treated as a temperature-dependent quantity and does not explicitly account for time dependence or stochastic freezing unless additional kinetic assumptions are introduced. For cirrus-relevant deposition nucleation or PCF, dependence on ice supersaturation must also be included (Hoose et al., 2012; Knopf et al., 2023; Murray et al., 2012)

Pore condensation and freezing

The Kelvin equation introduced in Section 2.1.1 describes the effect of interface curvature on equilibrium vapor pressure. For a convex liquid–vapor interface, curvature increases the equilibrium vapor pressure relative to a flat surface. Smaller droplets therefore require higher saturation ratios for equilibrium.

The opposite behavior occurs for a concave liquid–vapor interface, such as liquid water confined within a pore on an aerosol particle. If the radius of curvature is defined as

$$r_{\text{concave}} = -r, \quad (2.38)$$

substitution into the Kelvin equation gives

$$\ln S = \frac{2\sigma v_m}{r_{\text{concave}} k_B T} = -\frac{2\sigma v_m}{r k_B T}. \quad (2.39)$$

Consequently,

$$\ln S < 0, \quad (2.40)$$

and therefore

$$S = \frac{p}{p_0} < 1, \quad (2.41)$$

with p denoting the vapor pressure over the curved (concave) surface and p_0 denoting that over a flat surface. Thus,

$$p < p_0. \quad (2.42)$$

A concave interface can therefore support condensation at vapor pressures below the saturation vapor pressure over a flat interface. This behavior is commonly referred to as the inverse Kelvin effect or capillary condensation (Marcolli, 2014; Marcolli, 2020). It provides the thermodynamic basis for PCF, in which water condenses within pores before subsequently freezing under sufficiently low-temperature conditions (see Section 1.2).

2.2.3 Parameterizing ice nucleation in atmospheric models

Ice nucleation occurs on spatial and temporal scales much smaller than those resolved by numerical weather prediction and climate models. It must therefore be represented through parameterizations in cloud microphysics schemes (Hoose et al., 2012; Murray et al., 2012; Pruppacher et al., 1997). In cirrus clouds, this representation is particularly important because the number of ice crystals formed controls cloud optical properties, lifetime, and scattering of visible light (Burrows et al., 2022).

Most cirrus microphysics schemes consider both homogeneous and heterogeneous ice formation. In models, homogeneous freezing is commonly parameterized as a function of temperature, cooling rate, or updraft velocity, and ice supersaturation (Barahona et al., 2009; Kärcher et al., 2006; Kärcher et al., 2002). Because it can produce high ice crystal number concentrations over short timescales, homogeneous freezing strongly influences cirrus optical depth and radiative impact (Barahona et al., 2009; Kärcher et al., 2002).

Heterogeneous ice nucleation in cirrus clouds is important not only as an additional source of ice crystals, but also because it can modify the onset of homogeneous freezing. Ice crystals that form heterogeneously grow by vapor deposition and deplete water vapor, thereby reducing ice supersaturation. If this depletion is strong enough, homogeneous freezing may be delayed or suppressed (Barahona et al., 2009; Kärcher et al., 2006; Kärcher et al., 2002). The resulting clouds often contain fewer but larger ice crystals, which affects sedimentation, persistence, and radiation (Burrows et al., 2022; Hoose et al., 2012; Murray et al., 2012).

A simple representation of heterogeneous ice nucleation at mixed-phase cloud temperatures is to prescribe the concentration of active INPs diagnostically as a function of temperature,

$$N_{\text{INP}}(T) = f(T), \quad (2.43)$$

where $f(T)$ is derived from laboratory or field observations (DeMott et al., 2010; Hoose et al., 2012; Murray et al., 2012; Ullrich et al., 2017). Such diagnostic formulations are computationally efficient, but they do not explicitly account for aerosol composition, size distribution, mixing state, transport history, or aging (Hoose et al., 2012; Murray et al., 2012; Phillips et al., 2008). More aerosol-aware parameterizations instead relate ice nucleation to properties of the aerosol population, such as particle number, surface area, or composition (Niemand et al., 2012; Phillips et al., 2008; Ullrich et al., 2017). These approaches are better suited for cirrus applications because upper-tropospheric aerosol populations can vary strongly in space and time, influencing whether heterogeneous nucleation competes with or suppresses homogeneous freezing (Barahona et al., 2009; Hoose et al., 2012; Kärcher et al., 2006).

In the singular or active-site view, freezing is controlled by the presence of surface sites that become active at a given temperature (Connolly et al., 2009; Vali et al., 2015). This concept motivates the surface-area-based formulations introduced above, in which the expected number of active sites at cirrus conditions is written as

$$N_{\text{act}}(T, S_{\text{ice}}) = n_s(T, S_{\text{ice}})A_{\text{tot}}, \quad (2.44)$$

where $n_s(T)$ is the INAS density and A_{tot} is the total surface area of the relevant aerosol population (Connolly et al., 2009; Niemand et al., 2012; Ullrich et al., 2017). In contrast, stochastic descriptions treat freezing as a time-dependent process. For a particle surface area A exposed over a time interval Δt , the freezing probability can be written as

$$P = 1 - \exp(-JA\Delta t), \quad (2.45)$$

where J is the heterogeneous ice nucleation rate coefficient. This formulation links freezing probability to particle properties, thermodynamic conditions, and exposure time (Pruppacher et al., 1997; Vali et al., 2015).

Temperature-dependent active-site formulations are efficient and widely used, whereas time-dependent formulations can better represent cases in which residence time, transient supersaturation, or rapid vertical motion influence ice formation (Knopf et al., 2018; Knopf et al., 2023; Vali et al., 2015). In practice, modern parameterizations often combine empirical constraints with physically motivated dependencies on aerosol surface area, composition, and thermodynamic state (Knopf et al., 2018; Niemand et al., 2012; Phillips et al., 2008; Ullrich et al., 2017).

Overall, the representation of primary ice nucleation in atmospheric models has moved away from simple temperature-only descriptions towards aerosol-aware and process-based formulations (Hoose et al., 2012; Knopf et al., 2023; Murray et al., 2012; Vali et al., 2015). Remaining uncertainties arise from unresolved vertical motion, secondary ice production processes, poorly constrained upper-tropospheric aerosol populations, and the competition between homogeneous and heterogeneous freezing (Barahona et al., 2009; Burrows et al., 2022; Kärcher et al., 2006). These uncertainties directly affect simulated ice crystal number concentration, cloud optical properties, sedimentation, lifetime, and radiative forcing (Burrows et al., 2022; Hoose et al., 2012; Murray et al., 2012).

3 Methods

The facilities and instruments used in the studies presented in this thesis are described in this chapter. First, the Aerosol Interaction and Dynamics in the Atmosphere (AIDA) facility at the Karlsruhe Institute of Technology (KIT) and its associated instrumentation are introduced (Section 3.1), followed by a description of the Cosmics Leaving Outdoor Droplets (CLOUD) facility at European Organization for Nuclear Research (CERN) and its key instrumentation used for the experiments discussed here (Section 3.2). Section 3.3 introduces the working principle and implementation of the Continuous Flow Diffusion Chambers (CFDCs), which were employed at both the AIDA and CLOUD facilities. Finally, Section 3.4 discusses exemplary experiments that demonstrate the typical AIDA and CFDC ice nucleation measurement procedure.

3.1 The Aerosol Interaction and Dynamics in the Atmosphere (AIDA) facility

The AIDA facility comprised the AIDA atmospheric simulation chamber and the Aerosol Preparation and Characterization (APC) chamber, equipped with an independent suite of aerosol instrumentation. The AIDA chamber was operated from 1997 until its shutdown in 2025 and will be replaced by Aerosol Interaction and Dynamics in the Atmosphere cold and clean (AIDA_{c2}), which will offer more advanced scientific capabilities. In more recent project reports, the dismantled AIDA chamber is referred to as the "classic" AIDA chamber, AIDA_c, but the simple label "AIDA" will be used throughout this thesis. A detailed description of the chambers and instrumentation is provided in the following section.

3.1.1 The AIDA chamber

The AIDA chamber was an aluminum vessel with a volume of 84 m³, housed within a thermostatic enclosure that could be operated at temperatures ranging from 183 K to 333 K (Möhler et al., 2003; Möhler et al., 2005; Möhler et al., 2008) (Fig. 3.1). Air ventilation through heat exchangers inside the housing allowed the chamber temperature to be controlled with an accuracy of ± 0.3 K. The AIDA chamber temperature reported in this thesis was the arithmetic mean of temperatures reported by four thermocouples located at different heights within the chamber. A fan located in the bottom part of the chamber volume ensured the mixing of aerosols introduced, resulting in homogeneous conditions during the experiments.

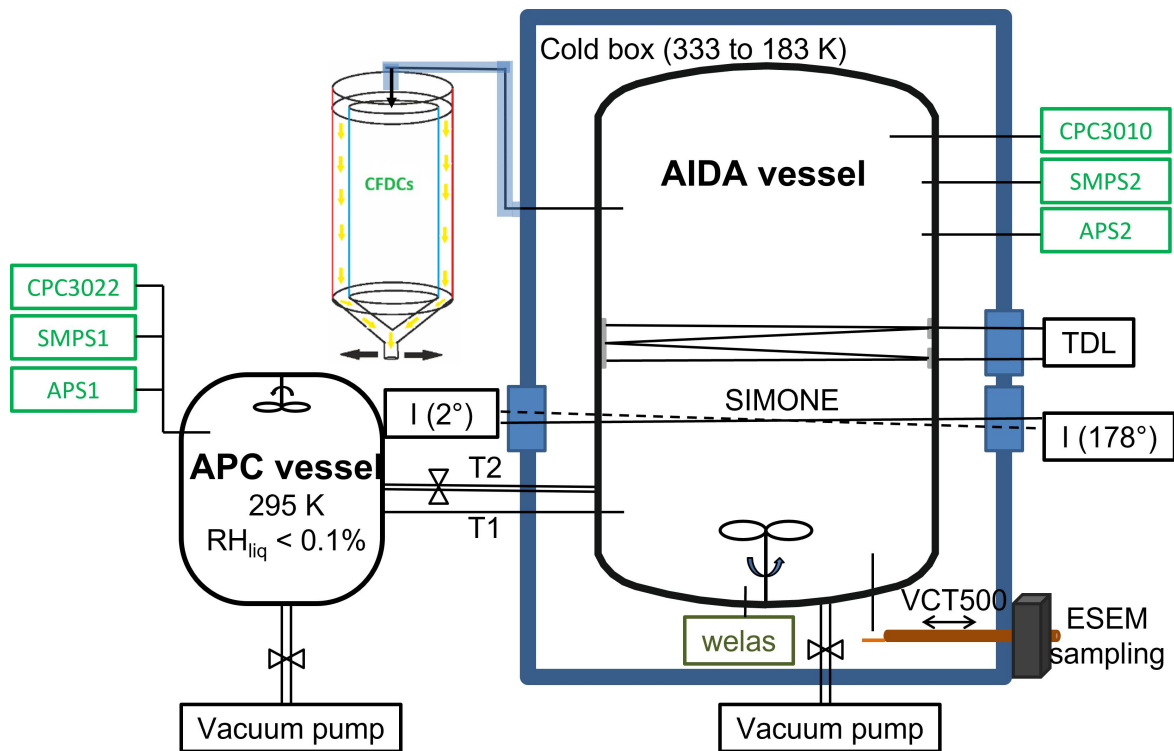


Figure 3.1: Schematic overview of the AIDA facility. The experiments presented in this thesis used selected components of the facility according to their specific requirements, as discussed in the relevant sections. Adapted from Wagner et al. (2024) with slight modifications.

Before each experiment, the chamber was cleaned by repeated evacuation and refilling cycles using particle-free dry synthetic air. During evacuation, the pressure was reduced to approximately 0.1 hPa by two mechanical vacuum pumps located beneath the chamber. This procedure reduced the background particle concentration to as low as $\approx 0.1 \text{ cm}^{-3}$ prior to each experiment. Before refilling the chamber with dry synthetic air, purified water from a GenPure Pro UV ultrapure water system (Thermo Scientific) was evaporated into the evacuated chamber to establish the desired relative humidity (RH) conditions. For dedicated expansion experiments investigating the ice nucleation activity of aerosol particles, a thin ice layer on the inner chamber walls was used to maintain initially ice-saturated conditions and to provide a source of water vapor during expansion, as described in detail in Section 3.4. Humidification was usually carried out in a warm environment, after which the chamber was cooled overnight to the desired initial temperature for the planned experiment.

The water vapor partial pressure, p_v , was continuously monitored using the Tunable Diode Laser (TDL) absorption spectrometer AIDA PCI in-cloud Tunable diode laser (APicT). This in situ optical instrument measured the intensity of a rotational–vibrational water vapor absorption line at $1.37 \text{ }\mu\text{m}$. The RH was calculated from the measured water vapor partial pressure using the formulations of Murphy et al. (2005), with an uncertainty of $\pm 5\%$ (Fahey

et al., 2014). The saturation ratio with respect to liquid water, S_{liq} , and the saturation ratio with respect to ice, S_{ice} , were calculated as

$$S_{\text{liq}} = \frac{p_v}{p_{\text{sat,liq}}(T)} = \frac{RH}{100\%}, \quad S_{\text{ice}} = \frac{p_v}{p_{\text{sat,ice}}(T)}, \quad (3.1)$$

where T was the chamber temperature. Throughout this thesis, RH refers to relative humidity with respect to liquid water. When a distinction between the liquid and ice phases is required, S_{liq} and S_{ice} are used explicitly.

The saturation vapor pressures over liquid water and ice were calculated as functions of temperature using the parameterizations of Murphy et al. (2005):

$$\begin{aligned} \ln p_{\text{sat,liq}}(T) = & 54.842763 - \frac{6763.22}{T} - 4.21 \log(T) + 0.000367 T \\ & + \tanh(0.0415(T - 218.8)) \left(53.878 - \frac{1331.22}{T} \right. \\ & \left. - 9.44523 \log(T) + 0.014025 T \right), \end{aligned} \quad (3.2)$$

$$\ln p_{\text{sat,ice}}(T) = 9.550426 - \frac{5723.265}{T} + 3.53068 \log(T) - 0.00728332 T. \quad (3.3)$$

Optical measurements of aerosol particles and hydrometeors were performed using the Streulichtintensitätsmessungen zum optischen Nachweis von Eispartikeln (SIMONE) instrument (Schnaiter et al., 2012). A polarized and collimated laser beam ($\lambda = 488 \text{ nm}$) horizontally traversed the diameter of the AIDA chamber, corresponding to a path length of approximately 4 m. Light scattered from the chamber center was detected in the forward (2°) and backward (178°) directions using Perkin Elmer MP-1383 photomultiplier tubes.

Two optical parameters were used to characterize the SIMONE measurements: the forward-to-backward scattering ratio, σ , and the linear backscattering depolarization ratio, δ . Here, I^{2° denoted the scattering intensity measured in the forward direction, whereas I^{178° denoted the backscattered intensity. The backscattered light was further separated into components parallel and perpendicular to the incident laser polarization, denoted by $I_{\parallel}^{178^\circ}$ and $I_{\perp}^{178^\circ}$, respectively. The forward-to-backward scattering ratio was defined as

$$\sigma = \frac{I^{2^\circ}}{I_{\parallel}^{178^\circ} + I_{\perp}^{178^\circ}}, \quad (3.4)$$

and the linear backscattering depolarization ratio was calculated as

$$\delta = \frac{I_{\perp}^{178^\circ}}{I_{\parallel}^{178^\circ}}. \quad (3.5)$$

All scattering intensities were corrected for background signals measured in the particle-free chamber.

The standard particle counter instrumentation of the AIDA chamber consisted of a Condensation Particle Counter (CPC), Aerodynamic Particle Sizer (APS), and Scanning Mobility Particle Sizer (SMPS). A detailed description of each component of the particle instrumentation can be found in Section 3.1.3.

For selected experiments, complementary offline and single-particle analysis techniques were used. The **Environmental Scanning Electron Microscope (ESEM)** instrument, a Quattro S environmental scanning electron microscope from FEI/Thermo Fisher Scientific Inc., was used to investigate aerosol particle morphology during the AIDA cloud-processing experiments described in Chapter 5. The ESEM generated high-resolution images by scanning a focused electron beam across the sample surface. Interactions between the electron beam and the sample produced secondary and back-scattered electron signals, which provided information on particle morphology, surface structure, and composition.

To preserve particle morphology during sampling from the AIDA chamber and subsequent ESEM analysis, a vacuum cryo-transfer system, EM VCT500 from Leica, was used. This system maintained the samples under cryogenic conditions throughout the transfer process, from particle sampling to electron microscopic analysis (Wagner et al., 2017; Wagner et al., 2021). Its central component was a liquid-nitrogen-cooled transfer shuttle equipped with a silicon sample substrate. The shuttle was moved into and out of the AIDA cold box through a pneumatic airlock. Particle deposition onto the substrate was enhanced electrostatically by connecting the substrate to a high-voltage supply set to +2 kV, while the aerosol flow from the chamber was passed through a unipolar corona discharge device (CD, 2000 type A, Palas GmbH). After sampling, the aerosol particles were sputter-coated with 1.5 nm of Pt using an ACE600 sputter coater from Leica, while the sample temperature was maintained at 173 K.

The **Particle Analysis by Laser Mass Spectrometry-Next Generation (PALMS-NG)** instrument from Purdue University, Indiana, was used to obtain chemical-composition mass spectra of individual aerosol particles sampled from the AIDA chamber, as described in Chapter 4. PALMS-NG detected single particles by light scattering and determined their chemical composition using a Laser Desorption and Ionization (LDI) technique combined with dual time-of-flight mass spectrometers. This approach enabled measurements of both refractory and non-refractory particle components over a size range of approximately 0.1 μm to 10 μm .

During analysis, a UV pulse generated by a 193 nm excimer laser ablated and ionized the particle inside the ion-source region. The resulting ions were extracted by high-voltage electrodes and directed into a custom-built bipolar S-shaped time-of-flight mass spectrometer, where they were separated according to their mass-to-charge ratio, (m/z) (Jacquot et al., 2024).

3.1.2 The Aerosol Preparation and Characterization (APC) chamber

The APC chamber, a 4 m³ stainless steel chamber, located beside the AIDA chamber, was used to nucleate secondary organic aerosol (SOA) particles and served as a buffer volume for the cloud-processing experiments described in Chapter 5. It was operated at room temperature and under dark conditions. Continuous evacuation cycles with dry synthetic air, reducing the pressure to 1 hPa, were used to clean the APC vessel. A fan located at the top of the APC chamber maintained the homogeneity within the chamber. The APC chamber was connected to the AIDA chamber by a 25 mm diameter stainless-steel tube (labeled T1 in Fig. 3.1). This tube was used to transfer the SOA particles from the APC to the AIDA chamber. In its use as a buffer volume during cloud-processing experiments, the APC vessel was evacuated and the valve in the second, 100 mm diameter connection tube to the AIDA chamber (labeled T2 in Fig. 3.1) was opened at an appropriate time to induce a "super-expansion" by rapidly reducing the pressure in the AIDA chamber. The aerosols in the APC chamber were characterized using a CPC, APS, and SMPS, before their transfer to the AIDA chamber.

3.1.3 Aerosol instrumentation

Condensation Particle Counter

A CPC (model 3010, TSI) was used to measure the aerosol number concentrations in each chamber. Aerosols drawn from the chamber passed through a zone containing high concentrations of butanol vapor at elevated temperatures. As the flow then entered a cooler region, namely, the saturator or condenser zone, the now-supersaturated vapor condensed onto the particles, growing them to detectable sizes. These enlarged particles scattered light from a beam inside the counter, and the number of scattering events was recorded as the aerosol count (Kulkarni et al., 2011).

Particle size distribution

In order to assess the size distribution of the aerosols, different instruments, such as SMPS (model 3071, TSI) and APS (model 3321, TSI), were used to cover the full aerosol particle size ranges.

The unevenly charged aerosol particles sampled by the SMPS were neutralized to a known stable Boltzmann charge distribution by the aerosol neutralizer. These particles were then selected by their electrical mobility in a differential mobility analyzer (DMA). The selected particles were then counted with a CPC within the SMPS (Sioutas, 1999). Thus, the combination of the DMA and CPC within the SMPS was used to analyze the electrical mobility of charged particles in an electric field, from which particle diameters in the range

of 10 nm to 800 nm were determined. The volume-equivalent diameter D_p is related to the mobility-equivalent (or electrical mobility) diameter D_{me} through the dynamic shape factor χ :

$$D_p = \frac{D_{me}}{\chi}, \quad (3.6)$$

where χ accounts for particle non-sphericity (shape-related drag effects). For spherical particles $\chi = 1$, whereas $\chi > 1$ for aspherical particles.

The APS made use of aerosol aerodynamic mobility to measure the diameter of particles in the size range 0.5 μm to 20 μm . Particle velocity was measured by passing the particle through two laser beams, and the velocity was then related to its aerodynamic diameter, D_{ae} . The volume equivalent diameter was calculated as:

$$D_p = \sqrt{\frac{\chi}{\rho}} D_{ae}, \quad (3.7)$$

where ρ is the particle density in g cm^{-3} , and χ is the dynamic shape factor.

Because the SMPS and APS rely on different measurement principles, their data were converted to a common diameter definition before comparison. The volume-equivalent diameter, D_p , is defined as the diameter of a spherical particle with the same volume as the measured particle (DeCarlo et al., 2004). The size distributions measured by the SMPS and APS were therefore converted to volume-equivalent diameter to allow consistent analysis of aerosol particles of wider size distribution.

welas Promo

The aerosols and hydrometeors produced during the AIDA expansion experiments were quantified using two Optical Particle Counters (OPCs; models 2300 and 2500, weißlichtaerosolspektrometer (welas)). These instruments covered size ranges of 0.7 μm to 46 μm (OPC1) and 5 μm to 240 μm (OPC2) (Wagner et al., 2013). The intensity of light scattered by individual particles, together with an appropriate calibration curve, provided information on their optical diameter. The optical diameter of a particle is a function of its size, shape, and refractive index. From the number of particles detected within a given time interval and the known volume flow rate through the optical detection region, the particle number concentration was determined (Schmitt, 2014).

Both OPCs were mounted outside the AIDA chamber but inside the thermally controlled housing, ensuring nearly 100 % sampling efficiency. The welas OPCs operated at a scattering angle of 90° and used a white-light source with a broad, continuous wavelength spectrum (Umhauer et al., 2000). Employing white light reduces scattering oscillation features in the Mie calibration curve and results in a smooth, unambiguous scattering response. Consequently, dust and other coarse aerosol particles were reliably detected by OPC and assigned their

corresponding optical diameters. At higher ice saturation ratios reached during the expansion, the aspherical and growing ice crystals formed inside the chamber were measured in welas channels associated with larger optical particle sizes. Aerosols and ice crystals were separated in the analysis by applying a size threshold in the welas data.

3.2 The Cosmics Leaving Outdoor Droplets (CLOUD) experiment

The CLOUD experiment was initially established to investigate the relationship between Galactic Cosmic Rays (GCRs) and cloud formation; it has since evolved into a leading platform for research on atmospheric particle formation, ion recombination, lightning, and the related charge, and cloud processing studies (Kirkby et al., 2011; Kirkby et al., 2016; Kirkby et al., 2023). This experimental facility is based at the Proton Synchrotron (PS) at the CERN.

3.2.1 The CLOUD chamber

The CLOUD chamber is an electro-polished stainless steel vessel with a volume of 26.1 m^3 (Fig. 3.2). It is designed to achieve high standards of cleanliness, and is primarily used to study

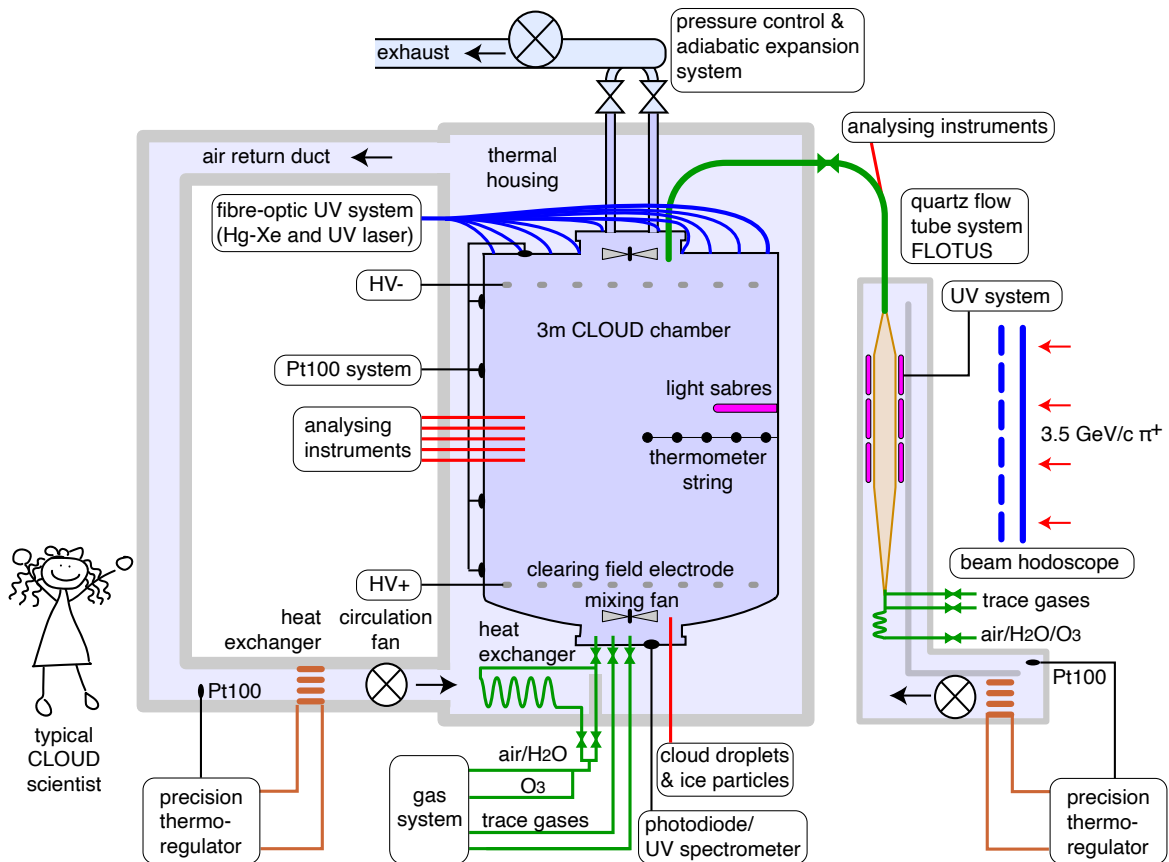


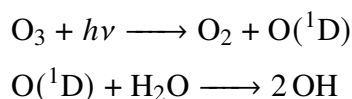
Figure 3.2: Schematic diagram of the CLOUD-FLOTUS setup (Courtesy: Jasper Kirkby).

atmospheric particle formation processes relevant from pristine regions to emission hot spots (Kirkby et al., 2016). It is placed within a thermal housing and has the ability to maintain a wide range of temperatures from $-70\text{ }^{\circ}\text{C}$ to $100\text{ }^{\circ}\text{C}$. The chamber temperature is controlled by regulating the temperature of the air circulating in the space between the chamber and the thermal housing. Under stable calibration conditions, the temperature uniformity is better than $\pm 0.06\text{ K}$ in the radial direction and $\pm 0.1\text{ K}$ in the vertical direction (Dias et al., 2017). The reported chamber temperature is measured using a horizontal string oriented radially near the midplane of the chamber and equipped with platinum resistance thermometers (Pt100). The chamber is maintained at an overpressure of 5 mbar relative to ambient pressure to prevent contamination by ambient air. Because CLOUD is operated in a continuous flush mode, synthetic air composed of nitrogen (79 %) and oxygen (21 %) is generated from cryogenic liquids and continuously introduced into the chamber during the experiments. This is referred to as the dry flow. A wet flow is generated by passing the dry air through a humidifier. The RH conditions within the chamber are derived from the dew point/ frost point measurements from a sampling dew point mirror (MBW Dew point mirror, model 973S) connected to it. The two counter-rotating and magnetically coupled fans made of stainless steel, mounted at the top and the bottom of the chamber, ensure the mixing of precursors and particles introduced into the chamber, and thereby establish a homogeneous distribution within the chamber (Voigtländer et al., 2012). The chamber can be operated at three conditions, namely the neutral, the GCR, and the beam stage. A high voltage of $\pm 30\text{ kV}$ is applied to generate electric field over the gas-aerosol mixture, thereby removing the ions to simulate the neutral conditions, whereas the chamber is exposed to the adjustable pion beam provided by the PS particle accelerator to induce the ion production during the beam stage. The experiments discussed in Chapter 6 of this thesis were conducted at GCR conditions during the CLOUD17 campaign.

To study nucleation and the properties of nucleated aerosol particles, precursor gases are usually generated using temperature-controlled evaporators and introduced into the chamber with a nitrogen carrier flow. More volatile compounds are injected directly into the chamber from gas cylinders. The precursor gases are introduced individually at the bottom of the CLOUD chamber, close to the main air inlet and just below the lower mixing fan. The light sources at the CLOUD facility consist of a UV fibre-optic system with four 200 W Hamamatsu Hg–Xe lamps, whose emission wavelengths span 250 nm to 450 nm; a krypton fluoride (KrF) excimer UV laser operating at 248 nm; and a set of four light sabres (LSs). Among the LSs–LS1, LS3, LS4, and LS5–LS1 and LS5 are low-pressure Hg lamps with an emission wavelength of 254 nm. LS1 consists of a single 52 W lamp, whereas LS5 consists of four 20 W lamps. LS3 and LS4 each comprise 48 high-power LEDs, with emission wavelengths of 385 nm and 528 nm, respectively.

All light systems are continuously monitored using a spectrometer and an array of photodiodes located at the bottom of the chamber. Dedicated actinometry experiments enable the quantitative determination of the actinic fluxes of the light systems at different intensities (Kupc et al., 2011).

Ozone is introduced into the chamber by passing O₂ through an ozone generator. Once the ozone concentration in the chamber has stabilized, the chamber lights are switched on to initiate the photolysis of O₃ and generate hydroxyl radicals, OH, in situ in the presence of water vapor supplied by a humidifier. The formation of OH proceeds via the photolysis of O₃ to electronically excited oxygen atoms, O(¹D), followed by the reaction of O(¹D) with water vapor:



Sampling probes with diameters of 0.5 inch and 1 inch are located along the mid-plane of the chamber, aligned with the centerline flow. Between experimental runs, the typical cleaning procedure for the CLOUD chamber involves operating the fans at 100 % efficiency to enhance mixing and facilitate the transport of vapors to the chamber walls, where they condense. In addition, a vertical electric field of ± 30 kV is applied using a pair of high-voltage electrodes. The mid-plane between the electrodes, which is at 0 V potential, coincides with the mid-plane of the chamber. Aerosol particles that are charged by atmospheric radiation, primarily GCR, are driven towards and accumulate near the electrodes upon exposure to the electric field generated by the applied high voltage. This procedure enables the rapid removal of ions and charged aerosol particles. These cleaning methods are used together with flushing the contents of the CLOUD chamber with particle-free air. When no new precursor gases or aerosol particles are introduced, the chamber contents are diluted over time by the continuous flow of clean synthetic air. The cleaning stage also includes preparing the chamber for subsequent experimental runs. This involves achieving the desired chamber temperature transition and setting the target humidity by regulating the wet and dry flows entering the CLOUD chamber.

Between experimental campaigns, the chamber walls are cleaned by rinsing them with ultrapure water at 100 °C for at least 24 h. During CLOUD17, and particularly during the experiments discussed in this thesis, the total dry flow maintained in the CLOUD chamber was 300 L min⁻¹.

3.2.2 The FLOW Tube System (FLOTUS)

The FLOW Tube System (FLOTUS) is an extension of the CLOUD experiment since November 2022 (Sommer et al., 2026). FLOTUS is used both to generate aerosols for subsequent injection into the CLOUD chamber and to supply slightly warmer, more humid

air through a port on the upper manhole of the CLOUD chamber to support cloud formation during cloud-processing experiments. FLOTUS is a 60 L quartz chamber with a length of 3 m and an internal diameter of 20 cm, designed to maintain laminar flow throughout its volume. It is equipped with an independent gas-handling system and temperature-control unit, allowing operation between -40°C and 100°C . Together with CLOUD, the FLOTUS system forms a pair of coupled but independently controlled experimental setups for studying atmospheric particle formation, growth, and chemical processing as well as other cloud-microphysical processes.

The output from FLOTUS is transferred into CLOUD through a wide-bore pipe via a remotely controlled gate valve (GV). The gas and aerosol streams in FLOTUS can also be sampled directly through a pickoff pipe, enabling measurements by instruments mounted on the upper platform. Hydroxyl radicals (OH) are produced in FLOTUS by photolysis of ozone under intense UV irradiation. Six low-pressure Hg UV lamps with a wavelength of 254 nm (lamps 1-6), arranged with three lamps on each side of the tube, can be operated individually to control radical production.

Since FLOTUS operates as a continuous-flow system, dry air is continuously supplied for cleaning and background flushing. The dry air is passed through a humidifier to generate a humid flow in FLOTUS, similar to the procedure used in CLOUD. A dew-point mirror connected to the system measures the dew point or frost point, from which the RH is calculated. In this thesis, FLOTUS was used as an aerosol generator for sulfuric acid solution droplets for the experiments discussed in Chapter 6. The aerosol generation procedure is described in the following section.

Aerosol generation in FLOTUS

A standard procedure was developed and followed for aerosol generation in FLOTUS and subsequent transfer to CLOUD. An air flow with constant concentrations of 64 ppb SO_2 and 300 ppb O_3 was added to FLOTUS maintained at 313 K and 13 % RH. The corresponding precursor concentrations were monitored using SO_2 and O_3 monitors connected to the chamber. Once the system had stabilized, the lower two UV lamps of FLOTUS (lamps 1 and 4) were switched on to initiate the formation of OH radicals and, consequently, the OH radicals thus formed react with the SO_2 to nucleate sulfuric acid solution droplets. Lamps 1 and 4, located at the bottom of FLOTUS, provided a comparatively longer residence time for the nucleated particles to grow by condensation and coagulation. The size distribution of the sulfuric acid solution droplets nucleated in this way is shown in the left panel of Fig. 3.3; this distribution was recorded by the long SMPS (lSMPS) connected to FLOTUS. The aerosol was then transferred to CLOUD through GV, where it exhibited unimodal lognormal size

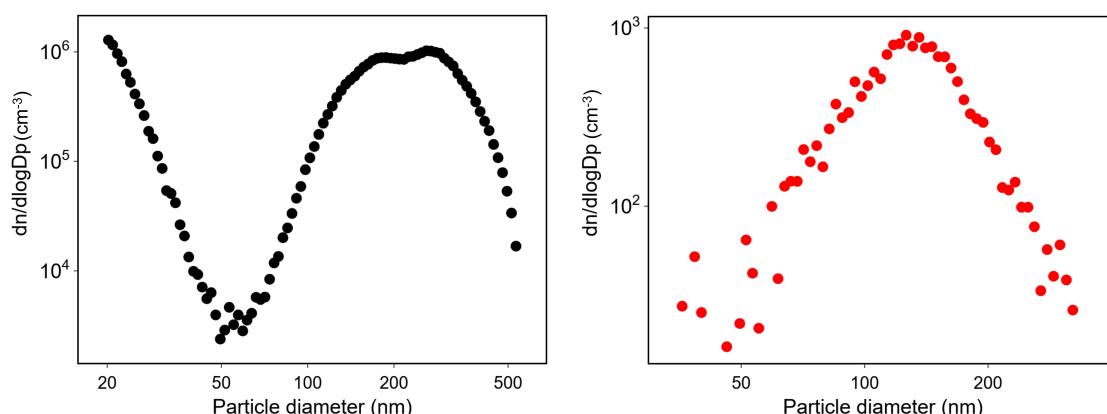


Figure 3.3: Aerosol size distributions measured from FLOTUS before introduction into the CLOUD chamber (left) and inside the CLOUD chamber (right). The measurements were obtained using the ISMPS connected to FLOTUS and combined nSMPS–ISMPS measurements connected from CLOUD.

distribution, as shown in the right panel of Fig. 3.3. The resulting aerosol population consisted of approximately $1000 \text{ particles cm}^{-3}$ with a median diameter of approximately 130 nm.

3.2.3 Instrumentation used during CLOUD17

The particle counters, precursor species and gas phase measurements used in this work are listed below, followed by a description of the particle phase measurements.

Table 3.1: Particle counters and aerosol sizing instruments used in this study.

Instrument	Purpose / Description
CPC 2.5 (TSI Model 3776)	Butanol condensation particle counter used to measure the total number concentration of particles with diameters larger than 2.5 nm.
nano SMPS (nSMPS)	Used to measure aerosol size distributions in the range 5 nm to 60 nm.
long SMPS (ISMPS)	Used to measure aerosol size distributions in the range 20 nm to 600 nm. A second ISMPS with the same size range was used to monitor aerosol sizes generated in the FLOTUS.

Table 3.2: Precursor gases and vapors used in this study.

Precursor / Species	Purpose / Description
Isoprene	Isoprene (PanGas, 1000 ppmv in N ₂) was supplied from pressurized cylinders and passed through a cryotrap at -53°C to remove low-volatility impurities, before its injection to CLOUD.
Glyoxal	Glyoxal was synthesized separately and introduced into the CLOUD chamber following Finkenzeller (2022). Dry glyoxal was produced by heating glyoxal trimer dihydrate with diphosphorus pentoxide (P ₂ O ₅) in slight excess (mass ratio 1.5:2). Diphosphorus pentoxide served to dehydrate the trimer, forming volatile glyoxal, which was collected in a cold trap at -97°C . Upon warming, the vapor pressure of glyoxal increased, and the compound melted at 283 K. The liquid glyoxal was then transferred into a 1 L stainless-steel cylinder. Dry nitrogen was added as a bath gas to maintain positive pressure, resulting in a gas mixture containing 1 % glyoxal by volume at a total pressure of 10 atm.

Table 3.3: Gas-phase measurement techniques used in this study.

Instrument / Species	Purpose / Description
Ozone monitor (Thermo Environmental Instruments, TEI 49C)	Used to monitor ozone concentrations in ppb. Separate instruments were connected to both CLOUD and FLOTUS.
SO ₂ gas monitor (Thermo Fisher Scientific Model 42i-TLE)	Used to measure SO ₂ concentrations, with a detection limit better than 0.5 ppb. The instrument was switched between FLOTUS and CLOUD during the experiments.
Quantum Cascade Tunable Infrared Laser Differential Absorption Spectrometer (QC-TILDAS) (Aerodyne Research, Inc.)	Used to measure ammonia gas concentrations based on the Beer–Lambert law by monitoring absorption at 967 cm^{-1} (Ellis et al., 2010; Moravek et al., 2019).

Instrument / Species	Purpose / Description
HORUS	Used to measure OH and HO ₂ radical concentrations. HORUS is a HydrOxyl Radical measurement Unit based on fluorescence Spectroscopy (Martinez et al., 2010).
H ₃ O ⁺ -PTR-MS	Used to measure isoprene concentrations, with a detection limit of approximately 50 ppt (Canaval et al., 2019; Graus et al., 2010).
Br-AIM-CIMS	Used for glyoxal and related gas-phase measurements using bromide chemical ionization at low pressure with active water feedback control.
Nitrate-CI-APi-TOF	Used to measure gaseous sulfuric acid and highly oxidized organic molecules. The nitrate-CI-APi-TOF is a time-of-flight mass spectrometer employing chemical ionization with nitrate ions. The ion source uses a corona discharge to generate primary ions from nitric acid clusters, (HNO ₃) ₀₋₂ NO ₃ ⁻ , which efficiently charge trace gases with very low volatility. The instrument was calibrated for gaseous sulfuric acid following Kürten et al. (2012); a transmission calibration allows concentrations to be derived for other masses (Heinritzi et al., 2016).

Particle phase measurements

Filter Inlet for Gases and AEROsols (FIGAERO): The chemical composition of the particles was measured using a FIGAERO coupled to a chemical ionization mass spectrometer (CIMS; Lopez-Hilfiker et al., 2014). Particles were sampled from the chamber onto a polytetrafluoroethylene (PTFE) filter with a pore size of 5 µm (Millipore-Sigma). The filter mass loading depended on the particle size distribution in the chamber, the collection flow rate (typically 7 L min⁻¹ to 8 L min⁻¹), and the total collection time. After particle collection, the filter was automatically moved in front of the ion-molecule reactor and aligned with a sealed port continuously flushed with pure nitrogen. The nitrogen stream was heated from room temperature to 180 °C using a programmed thermal desorption sequence controlled by EyeOn software (v2.1.4.5). As the filter temperature increased, low-volatility molecules partitioned back into the gas phase. The FIGAERO-CIMS was operated with I⁻ chemical ionization in a reduced-pressure ion-molecule reactor (approximately 120-150 mbar). Pure N₂ was passed around a CH₃I permeation tube (Vici) and through a ²¹⁰Po ionizer (NRD LLC)

to produce iodide ions. These highly polarizable ions readily formed adducts with oxygenated organic compounds, although a small fraction of interactions involved charge transfer between the ion and the neutral molecule.

Aerosol Mass Spectrometer: A high-resolution time-of-flight Aerosol Mass Spectrometer (HR-ToF-AMS; Aerodyne Research Inc.) was used to measure non-refractory PM_{2.5} (NR-PM_{2.5}) components, including organic aerosol, nitrate, sulfate, ammonium, and chloride, with a time resolution of 1 min (Canagaratna et al., 2007; DeCarlo et al., 2006; Williams et al., 2013). In the high-resolution time-of-flight Aerosol Mass Spectrometer (HR-ToF-AMS), sampled particles are focused into a narrow particle beam and vaporized on a resistively heated surface at approximately 500 °C to 600 °C. The resulting vapors are ionised by electron impact, and the ions are subsequently detected by mass spectrometry. This thermal-vaporization-based technique enables quantitative measurement of the particle-phase chemical composition of non-refractory aerosol components.

3.3 The Continuous Flow Diffusion Chambers (CFDCs)

General operating principle:

CFDCs are among the principal online instruments used to investigate the ice nucleation ability of aerosol particles. Both horizontal and vertical CFDC designs have been developed and applied in laboratory and field studies (DeMott et al., 2011; Garimella et al., 2016; Kanji et al., 2009; Rogers, 1988). In these instruments, aerosol particles are introduced into a narrow flow region bounded by ice-coated walls, where they are exposed to controlled temperature and humidity conditions.

The ice nucleation measurements presented in this thesis were mainly performed with mobile Ice Nucleation instrument of the Karlsruhe Institute of Technology (mINKA), a CFDC (Bertozzi, 2021). A small number of measurements were also conducted with Ice Nucleation instrument of the Karlsruhe Institute of Technology (INKA) (Schiebel, 2017). Both instruments were developed at KIT in cooperation with the Colorado State University and are based on the concentric cylindrical geometry and thermodynamic framework described by Rogers (1988).

In a CFDC with concentric cylindrical geometry, two ice-coated cylindrical walls are separated by a narrow annular gap. Each cylinder is made of copper and consists of cooled copper tubing attached to the inside of the inner cylinder and outside of the outer cylinder, both connected to an external chiller system (Proline, LAUDA), which can be operated over a temperature range from –70 °C to 20 °C. A cooling medium, such as ethanol when operated at AIDA, or thermal oil when operated at CLOUD, is circulated through the tubing to regulate the wall temperatures. By maintaining the inner and outer walls at different sub-zero temperatures,

a radial temperature gradient is established across the chamber. Hereafter, the inner and outer walls are referred to as the cold wall and the warm wall, respectively.

Because the saturation vapor pressure of water strongly depends on temperature, this temperature gradient, along with the water vapor gradient, produces gradients in water vapor partial pressure and saturation ratio according to the Clausius-Clapeyron relation (see Eq. (2.21)). Thus, the thermodynamic conditions experienced by the aerosol particles can be controlled by adjusting the temperatures of the two ice-coated walls.

Aerosol lamina and thermodynamic conditions:

The aerosol sample flows through the annular gap between the ice-coated walls. To ensure that sampled particles experience nearly identical thermodynamic conditions, the aerosol flow is confined to a narrow lamina within the overall laminar flow. Typically, the aerosol flow accounts for only about 5-10 % of the total flow, which consists of the aerosol flow together with particle-free dry synthetic air. The total flow is usually in the range of 10.0 std L min⁻¹ to 12.5 std L min⁻¹.

The radial position of the aerosol lamina depends on the wall temperature difference, the chamber gap width, the total flow rate, and the aerosol flow rate. This position is calculated according to Rogers (1988) and is illustrated in Fig. 3.4.

As shown in Fig. 3.4, higher ice saturation ratios can be achieved by increasing the wall temperature difference, ΔT , while maintaining a constant aerosol lamina temperature. However, larger values of ΔT also enhance buoyancy effects and may induce convective instability (Richardson, 2009). In particular, a downward negatively buoyant velocity component can develop in addition to the main laminar flow, as shown for $\Delta T = 14$ and 16°C in Fig. 3.4. Under such conditions, the aerosol lamina is no longer well constrained, and particles may experience non-uniform thermodynamic conditions (Garimella et al., 2017). Therefore, although there is no strict theoretical upper limit, there is a practical limit to the maximum ice saturation ratio that can be achieved in CFDC.

Design of mINKA and INKA:

Although mINKA and INKA operate according to the same basic principle, they differ in several design aspects that affect their operating ranges and experimental applications. mINKA was first described by Bogert (2020) and further detailed by Bertozzi (2021), whereas INKA was first described by Schiebel (2017). The main differences between the two instruments are their chamber lengths, particle residence times, and the presence or absence of an evaporation section. A detailed comparison and calibration of these instruments can be found in Bertozzi (2021).

The copper cylinders of INKA and mINKA are 150 cm and 85 cm long, respectively. Each instrument is equipped with 24 T-type thermocouples attached to the inner and outer cylinder walls. The thermocouples have an uncertainty of approximately ± 0.5 K. Because the cooling

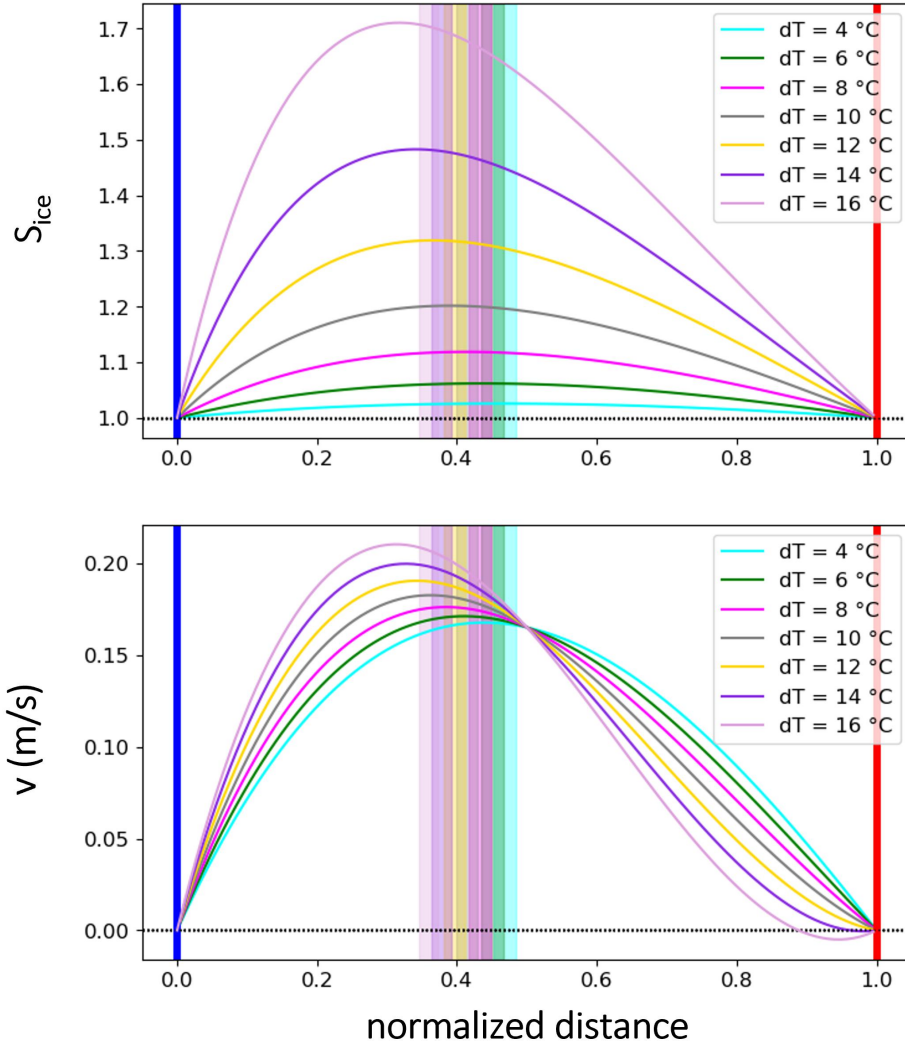


Figure 3.4: Ice saturation ratio (upper panel) and flow velocity (lower panel) experienced by sampled aerosols inside the CFDC. The blue bar on the left represents the cold (inner) wall, and the red bar on the right represents the warm (outer) wall. The shaded regions near the center indicate the position of the aerosol lamina for the indicated wall temperature differences.

liquid flows upward from the lower part of the cylinders, the effective cooling exhibits a vertical gradient. Based on calculations by Bertozzi (2021) and Schiebel (2017), the temperatures measured by the uppermost thermocouples in mINKA and INKA, respectively, are higher than those reported by the other thermocouples and, therefore, are not used to estimate the ice saturation conditions to which the sampled aerosols are exposed.

Unlike mINKA, INKA includes an evaporation section located in the lower third of the instrument. In this region, both walls are held at the same temperature as the warmer outer wall. Under these conditions, the gas phase is subsaturated with respect to liquid water, while the ice-coated walls maintain $S_{\text{ice}} = 1$. This section is particularly important for experiments

under mixed-phase cloud conditions, where supercooled droplets and ice crystals may coexist. Liquid droplets evaporate in the evaporation section, whereas ice crystals continue to grow, facilitating their identification and detection at the chamber outlet.

Droplet breakthrough is an important limitation in CFDCs. It can happen when experiments reach or go above water saturation. In this case, liquid droplets may survive the evaporation section and enter the optical detector, where they can be misclassified as ice crystals. For cirrus-cloud measurements, this is usually treated as a measurement artifact rather than a real atmospheric process. These experiments are normally done below liquid-water saturation but above ice saturation. Therefore, droplet breakthrough mainly limits the highest humidity range where ice nucleation data can be trusted. mINKA was designed mainly for studying ice nucleation under cirrus conditions. Accordingly, mINKA is operated under water-subsaturated conditions and at or above ice saturation.

Ice coating and chamber preparation:

Before measurements, the chamber is evacuated using a vacuum pump. In INKA, pressures of about 1 mbar can be reached, with a pressure change below 2 mbar per minute. In mINKA, the minimum achievable pressure is about 150 mbar because of a leak at a weld joint in the inner wall. It was not possible to fix this leak, and therefore, the chamber was continuously flushed with dry synthetic air while evacuating the chamber using the vacuum pump so as to reduce the intrusion of ambient air through this leak.

After evacuation, the chamber walls of mINKA and INKA are coated with ice. For this procedure, nanopure water is introduced into the chamber from below while the walls are held at a sub-zero temperature, typically around -27.5°C . The water introduced from beneath the chamber forms an ice layer on the cold walls, while excess water drains by gravity. The chamber is then evacuated again for about five minutes to smooth the ice layer. Considering the leak in mINKA, the ice formed on the inner wall can temporarily seal the leak. However, if the chamber is fully evacuated during the icing, the leak may reopen. For this reason, a continuous flow of 5 std L min^{-1} of particle-free dry synthetic air is maintained during the evacuation after the icing procedure.

During the icing procedure, the annular gap width decreases from 1.14 cm before icing to about 0.99 cm after icing. However, an average value of 1.06 cm is used in the calculations because the ice layer gradually deteriorates during the course of an experiment (Schiebel, 2017).

Measurement configuration:

A schematic diagram of mINKA is shown in Fig. 3.5. The sheath air is supplied from a synthetic-air source and mixed with the aerosol sample before entering the chamber. Inside mINKA, the aerosol particles are exposed to controlled ice-supersaturated conditions, which may lead to ice nucleation.

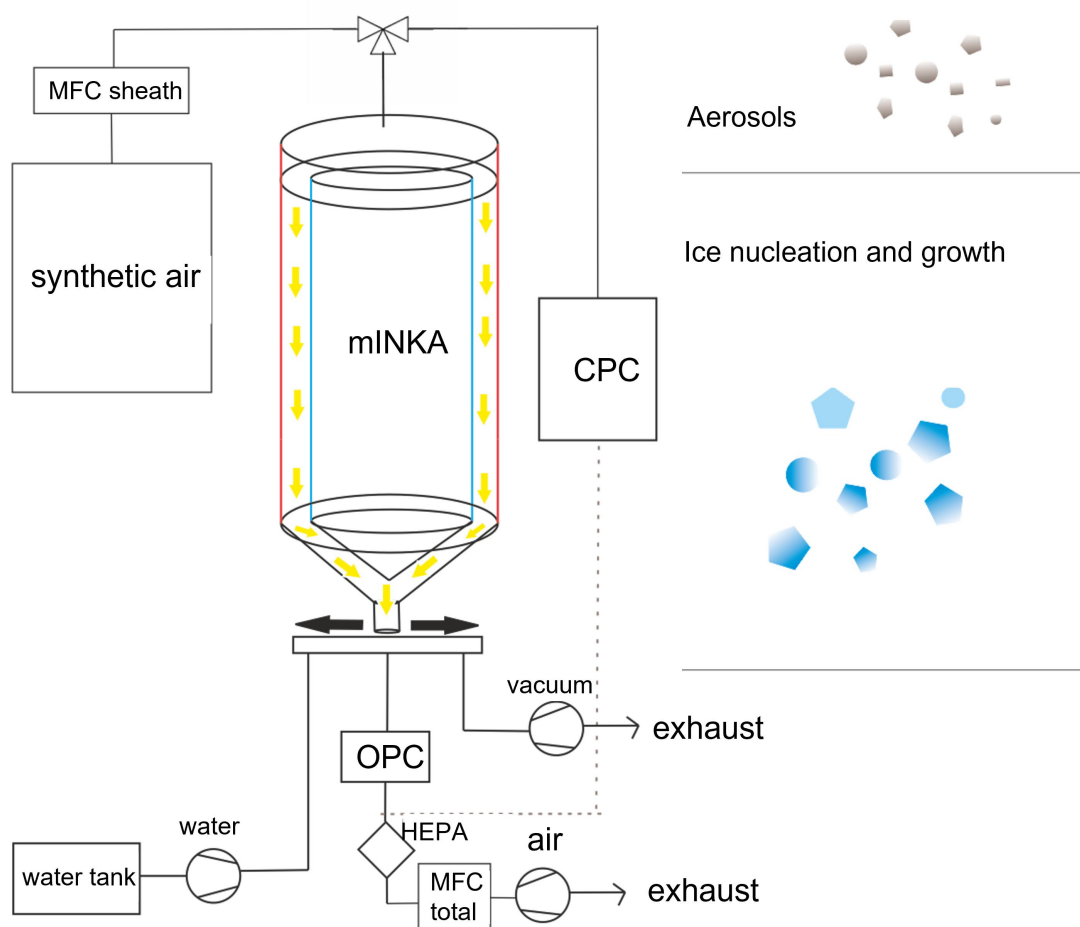


Figure 3.5: Schematic representation of the mINKA CFDC and associated flow configuration. Aerosol particles are introduced into the chamber together with particle-free sheath air and follow a confined laminar flow path between the ice-coated walls, indicated by the yellow arrows. Under ice-supersaturated conditions, activated particles nucleate and grow into ice crystals, which are detected by the OPC at the chamber outlet. A fraction of the aerosol flow is branched downstream of the inlet and directed to the CPC, which is operated in parallel to the CFDC chamber and measures the total aerosol number concentration used for normalization of the ice crystal number concentration.

Depending on the operational stage, the chamber outlet can be connected to three different lines: the vacuum line, the water reservoir used for ice coating, or the Climec OPC used during measurements. During measurements, the outlet of the CFDC is connected to a Climec OPC (CI-3100; Schiebel, 2017). The OPC measures the concentration of aerosol particles or hydrometeors leaving the chamber in size bins corresponding to their optical diameters. It is therefore used to determine the ice nucleation activity of the sampled aerosol.

A CPC (TSI model 3772) is connected to a separate branch downstream of the aerosol inlet and operated in parallel to the CFDC chamber. It measures the total aerosol number

concentration entering the system. This concentration is used to normalize the optical signal measured by the OPC at the chamber outlet.

The aerosol sample either enters the chamber directly or passes through a HEPA filter (Whatman) before entering. The filtered line is used periodically during experiments to determine the background signal of the OPC. The wall temperatures and mass flow rates, and therefore the aerosol lamina temperature and RH, are controlled by a home-built LabVIEW program.

Optical detection and data evaluation:

Within the OPC, each particle scatters light, and the resulting scattering intensity is detected and amplified in the range 0.05 - 4.50 V. These signals are grouped into 20 logarithmically spaced bins, from which the particle number concentration dn in each bin is calculated. To suppress electrical noise, a lower detection limit can be applied during OPC data processing.

The ice crystal number concentration is determined by applying an additional signal threshold, here referred to as the ice threshold. Particles with scattering intensities above this threshold are classified as ice crystals, whereas particles below it are interpreted as non-activated aerosol particles. As for the other OPC used in this thesis, the concentration uncertainty of the OPC is assumed to be 20 % (Bertozzi, 2021; Wagner et al., 2013).

The choice of the ice threshold is critical and must be evaluated separately for each experiment. For the measurements presented in this thesis, which were generally performed at $S_{liq} < 1$ and low temperatures, the ice threshold was chosen as the lowest signal intensity that excluded most of the aerosol background. Before each CFDC measurement, some counts above this threshold can occur because of large aerosol particles or ice fragments detached from the chamber walls. This contribution is treated as background. To correct for it, the average number concentration measured above the ice threshold before the start of each RH scan is subtracted from the total ice crystal number concentration. A standard RH scan is described in detail in the next section.

Finally, the ratio of the ice crystal number concentration to the total aerosol number concentration gives the fraction of aerosol particles that nucleated ice, hereafter referred to as activated fraction (AF). The ice nucleation onset values calculated from the CFDC measurements discussed in this thesis are typically defined as the temperatures and ice saturation ratios at which 0.1 % of the aerosol particles have nucleated ice.

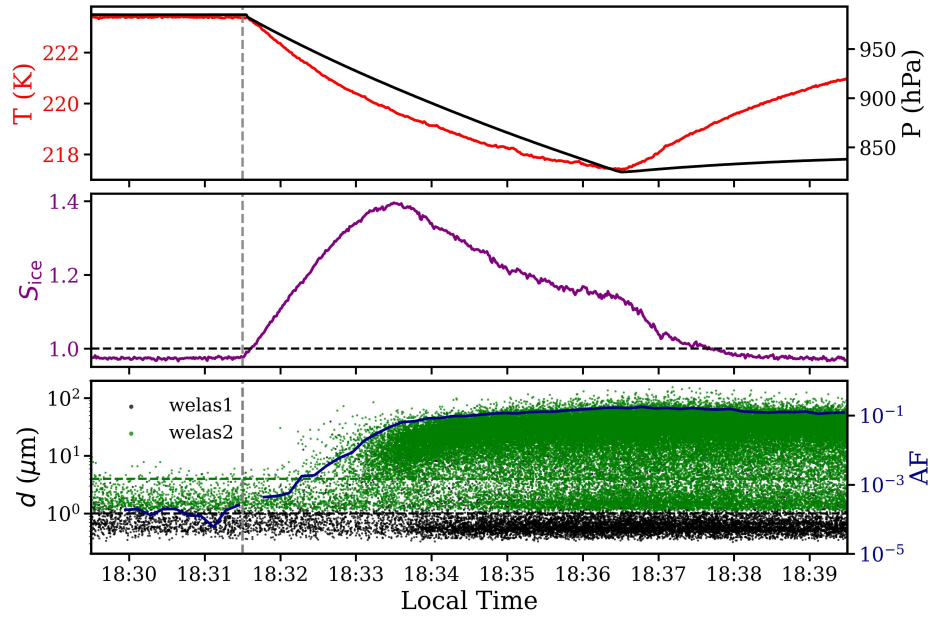
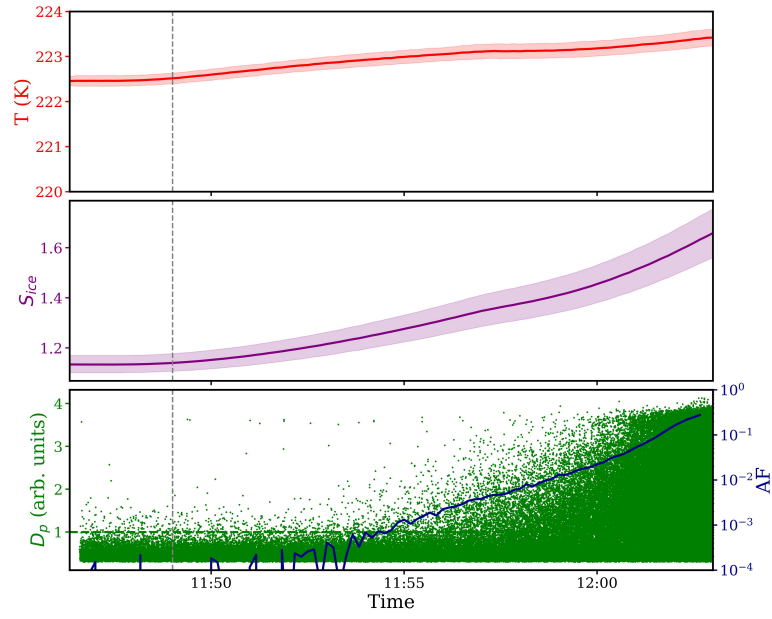


Figure 3.6: Illustration of a typical AIDA expansion experiment. The upper panel shows the mean temperature T in Kelvin (red line) together with pressure (black line). The middle panel shows the temporal evolution of the ice saturation ratio S_{ice} derived from TDL absorption spectroscopy; the black dashed line indicates $S_{ice} = 1$. The lower panel presents the single particle scattering data from the welas OPC. The activated fraction (AF) is indicated on the corresponding right y-axis. The vertical dashed gray line marks the start of the AIDA expansion.

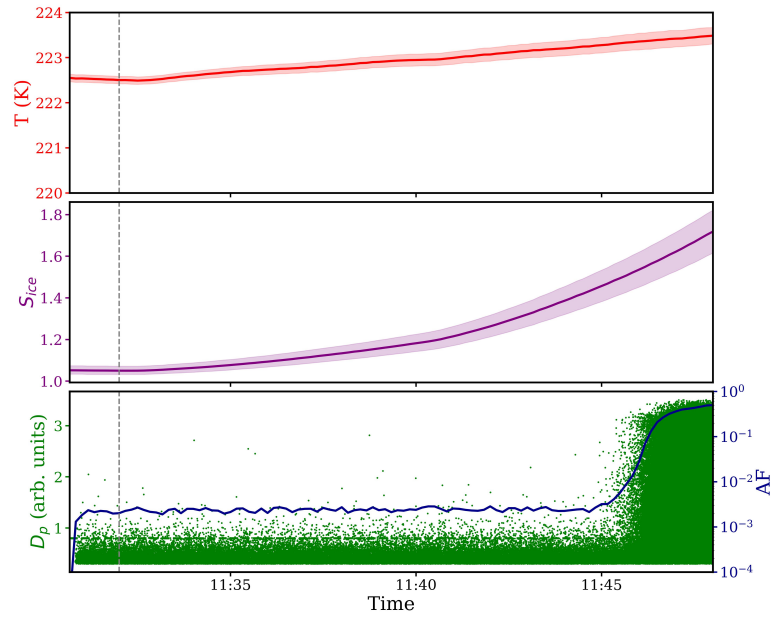
3.4 Typical experimental procedure of chamber expansion experiment and CFDC measurements

Typical examples of an AIDA expansion experiment, a mINKA scan, and an INKA scan are shown in Fig. 3.6 and Fig. 3.7. In all experiments, K-feldspar particles were used as the seed aerosol particles.

Fig. 3.6 illustrates a standard expansion experiment using the AIDA chamber to investigate the ice nucleation activity of aerosols at an initial chamber temperature of 223 K. The upper panel shows the aerosol-gas temperature on the left axis and the chamber pressure on the right axis. The middle panel shows the evolution of the saturation ratio with respect to ice, calculated from the TDL measurements using the parameterization of Murphy et al. (2005) (see Eq. (3.3)). The lower panel shows the single particle optical data measured by the welas OPCs, whereas the activated fraction, AF, is presented on the right y-axis of the same panel. The vertical dashed gray line marks the reference time, corresponding to the start of the expansion experiment.



(a) Typical mINKA scan.



(b) Typical INKA scan.

Figure 3.7: Comparison of typical mINKA and INKA scans. The upper panels show the mean aerosol temperature T in Kelvin, the middle panels show the temporal evolution of the ice saturation ratio, S_{ice} , experienced by the aerosol particles, and the lower panels present the single particle scattering data measured by the Climet OPC at the chamber outlet. The activated fraction (AF) is represented on the corresponding right y-axis. The shaded regions indicate the uncertainties in temperature and ice saturation ratio. The vertical dashed gray line marks the start of the humidity ramp.

Before an AIDA expansion experiment, the chamber is conditioned to near ice-saturated conditions due to the formation of a thin ice layer on the chamber walls (as already discussed in Section 3.1.1). During an AIDA expansion experiment, the chamber pressure is reduced using two mechanical pumps located beneath the chamber. This pressure decrease causes the gas volume (top panel, Fig. 3.6) to cool and consequently leads to increasing supersaturation with respect to ice (middle panel, Fig. 3.6). During this process, aerosol particles that are initially detected by the welas OPCs in the lower size channels nucleate ice crystals and are thereafter detected in higher size channels as their size increases due to ice crystal growth. A size threshold, indicated by the dashed horizontal lines in the lower panel of Fig. 3.6, is applied to distinguish unactivated aerosol particles from nucleated ice crystals.

Fig. 3.7 shows typical mINKA and INKA scans conducted at approximately 223 K. In each case, the upper panel shows the temperature experienced by the aerosol as it traverses the chamber, the middle panel shows the ice saturation ratio resulting from the imposed wall-temperature gradient, and the lower panel presents the single particle optical data measured by the Climet OPC at the chamber outlet.

Each CFDC scan, also referred to as a RH scan, is a procedure in which the sampled aerosol particles are exposed to increasing ice-supersaturation conditions ranging from $S_{ice} = 1.0$ to 1.8, while the temperature is kept constant. Each measurement takes approximately 15 minutes, with a rate of change in ice saturation ratio of $dS_{ice}/dt = 0.03 \text{ min}^{-1}$. This is followed by resetting the chiller temperatures before continuing with subsequent ice nucleation measurements. Although the uncertainty associated with CFDC measurements increases with increasing S_{ice} , repeated measurements performed under the same initial settings and icing procedure are considered highly precise, as the observed ice nucleation values are robust and reproducible.

4 Internal mixing of mineral dust particles with secondary inorganic and organic compounds

When atmospheric dust particles traverse from the boundary layer to the upper troposphere, they can become internally mixed through the condensation of low- or semi-volatile organic and inorganic compounds. This process is generally assumed to suppress the intrinsic heterogeneous ice nucleation ability of dust aerosols at cirrus temperatures by blocking the ice-active sites on their surface through the coating layer. However, it is also possible that the coating layer itself acts as an ice-active site, for example, when the phase state of the coating layer is transformed from liquid to solid through chemical processing. The experiments presented in this chapter expand our current understanding of the role of coatings on the heterogeneous ice nucleation activity of dust aerosol particles, with a special focus on the possibility that a change of the phase state of the coating layer from liquid to solid might "restore" the heterogeneous ice nucleation ability of the coated dust particles. Potassium feldspar (K-feldspar), identified as a particular ice-active mineralogical component, was used as the principal example mineral dust type in this study. A small number of experiments were also conducted with a field-collected Asian dust sample. The coating experiments made use of a combination of the Aerosol Interaction and Dynamics in the Atmosphere (AIDA) chamber and the Continuous Flow Diffusion Chamber (CFDC) instruments. The AIDA chamber acted as a reacting vessel to coat the pre-added K-feldspar particles in situ with various organic and inorganic compounds at a cirrus temperature of 223 K. Throughout the coating process, the CFDCs continuously monitored the change in the particles' ice nucleation ability.

Chapter 4 is structured as followed. In Section 4.1, relevant background information is provided, including the role of mineral dust particles as ice-nucleating particles (INPs) at cirrus conditions, the physicochemical changes dust particles undergo upon their transport from the boundary layer to the upper parts of the atmosphere, our current understanding of the effect of coating layers on the heterogeneous ice nucleation ability of dust particles under cirrus conditions, and the motivation for the new set of coating experiments discussed in this thesis. Section 4.2 describes the injection and characterization of the bare dust aerosol particles, followed by the experimental protocol for the injection of gaseous precursor compounds and reactants to initiate the coating process. The heterogeneous ice nucleation ability of bare K-feldspar particles is summarized in Section 4.3. Section 4.4 and Section 4.5 then focus on the CFDC measurements from the coating experiments. Section 4.4 summarizes

experiments in which the coating layer was either liquid (for inorganic materials) or highly viscous (for organic materials). These experiments generally led to a significant deterioration in the intrinsic heterogeneous ice nucleation ability of the K-feldspar particles. Section 4.5 describes experiments aimed at transforming a liquid inorganic coating layer into a solid one through the addition of ammonia. A summary of the results is presented in Section 4.6.

4.1 Background

4.1.1 Mineral dust particles as INPs under cirrus cloud conditions

Mineral dust particles are among the most ice-active aerosol types observed in the atmosphere, and they are frequently identified as a key source of INPs in the cirrus regime (Cziczo et al., 2013; Froyd et al., 2010; Froyd et al., 2022; Hoose et al., 2012; Kanji et al., 2008) as well as in the mixed-phase cloud regime (Boose et al., 2016; Hoose et al., 2012). Their importance arises from (i) their global abundance and efficient long-range transport, and (ii) the presence of crystalline substrates and surface features (cracks, pores, edges) that can host a limited number of highly active sites for ice formation (Hoose et al., 2012; Kanji et al., 2017; Murray et al., 2012). Consequently, mineral dust is often treated as the dominant source of cirrus relevant INPs in observations and models (Beer et al., 2022; Cziczo et al., 2013; Froyd et al., 2022).

Figure 4.1 summarizes laboratory measurements on the heterogeneous ice nucleation ability of a range of natural dust samples, pure minerals such as illite, kaolinite, and montmorillonite, as well as mineral dust proxies. At cirrus temperatures below 235 K, the ice nucleation onsets of the various dust particle types are typically well below the threshold for the homogeneous freezing of aqueous solution droplets, underlining their pronounced heterogeneous ice nucleation ability. A robust feature across studies is the strong dependence of the ice nucleation activity on particle size (or surface area) and on mineralogy (Boose et al., 2016; Hoose et al., 2012). Larger particles carry more active sites, increasing the probability of ice formation at a given supersaturation. In addition, differences in mineral composition across source regions (e.g., varying fractions of feldspars, clays, quartz, carbonates) can shift ice onset conditions substantially, such that “dust” does not represent a single, universal INP class (Boose et al., 2016; Welti et al., 2019). Nevertheless, efforts are being made to obtain a suitable “average” dataset to represent the heterogeneous ice nucleation ability of “mineral dust” in models, such as the Ullrich et al. (2017) parameterization. This was obtained by fitting a large set of ice nucleation measurements with various natural mineral dust samples from different desert regions in the AIDA chamber. On the microscopic level, however, studies with selected pure mineral components such as K-feldspar are pursued with unbroken interest to identify certain micro-textures or topographic features that could explain a superior ice

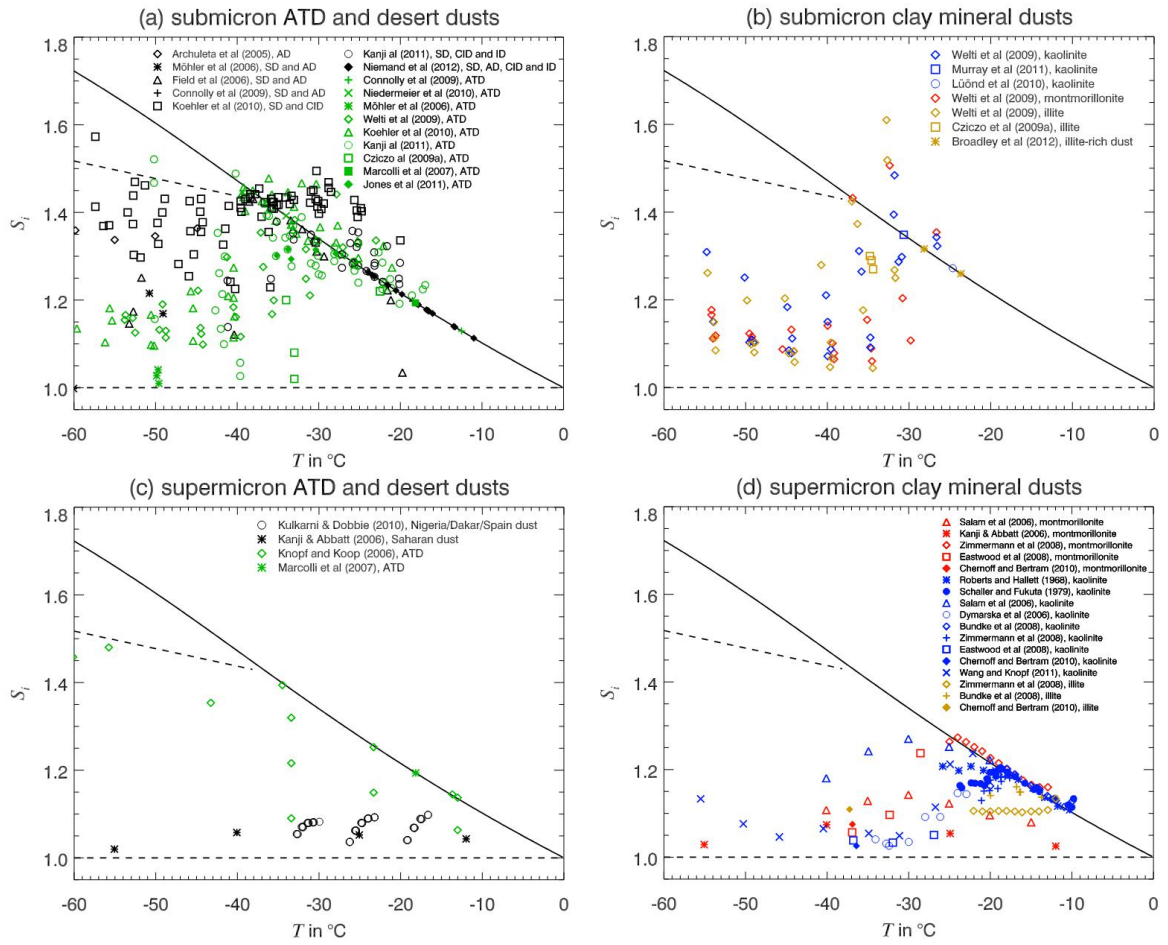


Figure 4.1: Ice nucleation onset temperatures and saturation ratios for several types of dust aerosol particles. (taken from Hoose et al. (2012), Fig. 3 therein)).

nucleation ability (Harrison et al., 2016; Kiselev et al., 2017; Whale et al., 2017). Beyond traditional deposition/immersion freezing descriptions, an increasing body of work suggests that what is often reported as ice nucleation in the deposition mode in dust at low temperatures can be explained by the pore condensation and freezing (PCF) mechanism, where water condenses in nanoscale cavities below water saturation (via the inverse Kelvin effect) and subsequently freezes at lower ice saturation ratios compared to droplets from aqueous solution (David et al., 2019). This framework connects the macroscopic ice nucleation activity of dust to its microstructural properties that are central to understanding cirrus-relevant ice nucleation. However, these microphysical properties may change during the transport of dust in the atmosphere, as particles become coated with secondary inorganic and organic materials.

4.1.2 Aging of dust aerosol particles during atmospheric transport

Field measurements consistently show that mineral dust is rarely present in the atmosphere as a purely "fresh" aerosol after regional-to-intercontinental transport. Instead, dust particles become internally mixed with inorganic and organic species. These can include sulfate from SO₂ oxidation, nitrate, ammonium, and secondary organic material (SOM), driven by heterogeneous chemistry, condensation, and coagulation (Cziczo et al., 2013; Fitzgerald et al., 2015; Froyd et al., 2010; Hoose et al., 2012; Jordan et al., 2003; Kanji et al., 2017; Li et al., 2009).

In particular, observations from diverse environments repeatedly identify nitrate associated with mineral dust, indicating that uptake of HNO₃ and related NO_x oxidation products is a common pathway of atmospheric dust aging (Fitzgerald et al., 2015; Froyd et al., 2010; Jordan et al., 2003; Li et al., 2009). Nitrate-coated dust is expected to be especially relevant in regions where deep convection efficiently transports boundary-layer pollutants to the upper troposphere. Continental convective systems enhance NO and NO₂ aloft through both lightning and vertical transport of anthropogenic emissions (Tie et al., 2002). As a result, nitrate-coated dust is likely common in strongly convective regions such as the Asian monsoon region. The acidic nitrate coating layer may be further processed and neutralized by ammonia (NH₃) to ammonium nitrate. Ppb levels of NH₃ have been observed over the Asian monsoon region (Clarisse et al., 2009; Van Damme et al., 2018), and satellite retrievals indicate enhanced ammonium nitrate in the upper troposphere (Höpfner et al., 2019). Cloud processing may further enhance ammonia partitioning to particles, since dissolved ammonia has low retention during freezing and can therefore provide an additional gas-phase source (Ge et al., 2018). Together with excess ammonium over China (Meng et al., 2020) and the elevated pH of alkaline mineral particles, these conditions can favor efficient formation and stabilization of ammonium nitrate on dust surfaces (Karydis et al., 2021; Nenes et al., 2020).

The distinction between acidic nitrate and neutralized ammonium nitrate coating is important because it may change the phase state of the coating layer. Whereas an acidic coating will likely be present as a liquid layer, its neutralization by ammonia offers a potential pathway for crystallization, forming a solid ammonium nitrate coating. For pure ammonium nitrate aerosol particles, efflorescence is strongly inhibited so that the particles remain non-crystalline even at low relative humidity (RH) and low temperature (Davis et al., 2015; Lightstone et al., 2000; Wagner et al., 2020). However, there are several pathways that could lead to heterogeneous efflorescence. One of these is the co-condensation of small amounts of sulfate into the particles. This easily crystallizes to form small solid "islands" of ammonium sulfate, triggering the precipitation of ammonium nitrate (Martin et al., 2003; Wagner et al., 2020; Wang et al., 2022). The detection of solid ammonium nitrate particles by Höpfner et al. (2019) mentioned above can likely be explained by this mechanism. Crystallization of ammonium

nitrate may also be facilitated by solid inclusions such as mineral dust (Han et al., 2002; Usher et al., 2003), implying that the phase state of atmospheric coatings may be closely coupled to the dust core. Likewise, this phase change may also occur for a sulfate coating layer, i.e., the transition from an acidic, liquid sulfuric acid coating layer to crystalline ammonium sulfate. The expected impact on the particles' ice nucleation ability will be discussed in Section 4.1.4.

Apart from inorganic species such as sulfate and nitrate, mineral dust particles may also get coated by organic material, e.g., by SOM. The following discussion addresses a specific precursor compound for SOM, namely isoprene, which has been the focus of recent field studies, modeling work, and dedicated laboratory experiments. Although previously considered to have a negligible impact on atmospheric aerosol particle concentrations, isoprene emissions in tropical rainforests and Asia have recently gained attention. Observations from in situ aircraft measurements over the Amazon rainforest revealed a significant contribution of isoprene to the aerosol particle load in the Amazonian upper troposphere (Curtius et al., 2024). These findings were further supported by chamber experiments at European Organization for Nuclear Research (CERN) Cosmics Leaving Outdoor Droplets (CLOUD), where Shen et al. (2024b) simulated various atmospheric conditions, including the effects of lightning, to investigate the role of isoprene in aerosol particle formation. Modeling studies discuss how isoprene is uplifted by deep convection and released along the cloud outflows over the Amazon region both in the presence and absence of nitrogen oxide radicals (Bardakov et al., 2021; Mayhew et al., 2023; Zha et al., 2023). Similar availability and transport of isoprene to high altitudes may occur in the Asian monsoon region (Fu et al., 2016). For example, the concentration of isoprene in India during the monsoon period was reported to levels of 1-2 ppb, which is comparable to tropical forests (Mishra et al., 2020). Surprisingly, the concentration of isoprene is highest in the monsoon period due to stronger biogenic emissions from the vegetation at high moisture conditions and also due to a lower ventilation coefficient (the ventilation coefficient is the product of boundary layer height and wind speed). The complex meteorological conditions over the monsoon region and the topography of the Himalayan foothills form an ideal condition for the rapid transportation of pollutants from the boundary layer to the upper troposphere. In addition to driving new particle formation, the low-volatility oxidation products of isoprene might also partially condense on pre-existing aerosol particles (Claeys et al., 2021), such as uplifted mineral dust grains. This would result in the formation of SOM-coated mineral dust particles. At low temperatures in the upper troposphere, the organic coating layer is likely in a highly viscous phase state (Lienhard et al., 2015; Schmedding et al., 2020).

4.1.3 Earlier studies on the ice nucleation ability of coated mineral dust particles under cirrus conditions

The preceding chapter has made it clear that many different chemical species can condense and form a coating layer on transported mineral dust particles. While the laboratory studies of fresh or “clean” dust shown in Section 4.1.1 emphasize the high intrinsic heterogeneous ice nucleation ability of mineral surfaces under cirrus conditions, atmospheric aging can substantially modify ice nucleation by (i) masking the active sites of ice nucleation, (ii) changing particle hygroscopicity and the pathway of water uptake, and (iii) partially filling pores/cavities that are relevant for PCF. Despite the ubiquity of coated dust particles, the number of previous ice nucleation studies with such particle types at cirrus temperatures are scarce, limited to a couple of case studies and one more comprehensive study as part of the Fifth Ice Nucleation Workshop – part 1, which was conducted at the AIDA chamber in 2014 (Bertozzi, 2021).

Among the earlier case studies, Archuleta et al. (2005) investigated bare and sulfuric acid-coated metal oxide particles at temperatures between 228 K and 213 K. At 228 K, the effect of the coating layer on the onset of ice nucleation was less than the measurement uncertainty. At 213 K, however, the different particle types reacted differently to the presence of a coating layer: for example, the ice nucleation onset decreased for iron oxide particles, but increased for aluminum oxide particles. Cziczo et al. (2009) found that Arizona test dust particles were strongly passivated when coated with sulfuric acid at 228 K. Eastwood et al. (2009) investigated the onset conditions for ice nucleation on bare kaolinite, sulfuric acid-coated kaolinite, and ammonium sulfate-coated kaolinite particles at temperatures between 246 K and 233 K. While the sulfuric acid coating significantly decreased the intrinsic heterogeneous ice nucleation ability of the kaolinite particles at all temperatures, the ammonium sulfate-coated kaolinite particles retained a high ice nucleation efficiency at 236 K. The coated particles were generated by nebulizing a suspension of kaolinite and the coating material in high-purity water. They were then deposited onto a glass slide at the bottom of a flow cell for the ice nucleation measurements, and were initially exposed at room temperature to $S_{ice} < 0.01$ in a dry He gas flow. While the sulfuric acid-coated particles remained liquid throughout the experiments, the ammonium sulfate coatings underwent efflorescence during initial conditioning at low S_{ice} . Therefore, the temperature-dependent ice nucleation ability of the ammonium sulfate-coated kaolinite particles mimics the behavior of pure, crystalline ammonium sulfate, representing a competition between deliquescence, followed by homogeneous freezing at the higher temperature of 246 K, and heterogeneous ice nucleation, which occurs before the deliquescence relative humidity (DRH) is surpassed at the lower temperature of 236 K (Abbatt et al., 2006; Bertozzi et al., 2024; Cziczo et al., 1999). The apparent “retention” of the intrinsic ice nucleation ability of the kaolinite particles with an

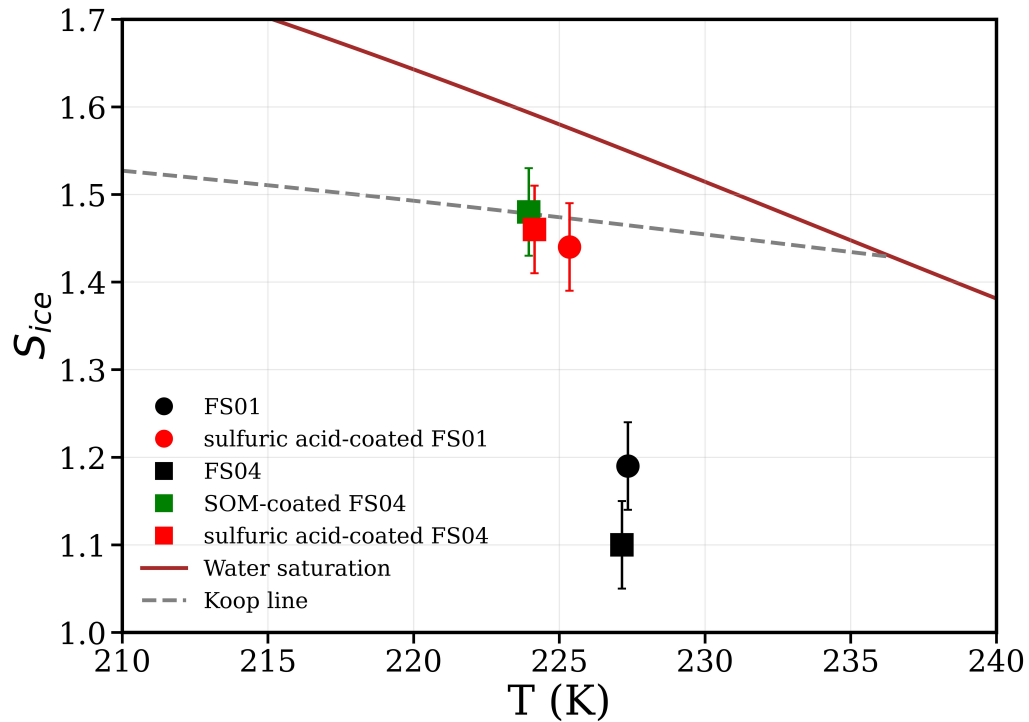


Figure 4.2: Ice nucleation onset conditions ($AF = 0.1\%$) for bare and coated K-feldspar particles at cirrus temperatures, inferred from AIDA expansion experiments during the FIN01 campaign (Bertozzi, 2021). Circles and squares represent two different types of K-feldspar particles, labeled FS01 and FS04, respectively. Black symbols represent the bare dust particles, whereas red and green markers indicate particles coated by sulfuric acid and SOM, respectively. The brown curve denotes the water saturation. The gray dashed line indicates homogeneous freezing conditions at 223 K (Koop et al., 2000).

ammonium sulfate coating at 236 K is, in fact, related to the coating layer acting as the ice nucleating entity itself. Coatings of SOM derived from the ozonolysis of α -pinene have been shown to shift the ice onset to higher ice supersaturation for mineral dust proxies and clay minerals at cirrus temperatures (Koehler et al., 2010; Möhler et al., 2008). The degree of deactivation depended on the amount of condensed organic material. No other organic precursor types than α -pinene have been used so far.

During the Fifth Ice Nucleation Workshop – part 1, two different types of K-feldspar particles (with labels FS01 and FS04) were subjected to controlled in situ coating procedures in the AIDA chamber at 228 K to coat them with small, atmospherically relevant amounts of sulfuric acid from the oxidation of SO_2 and SOM from the dark ozonolysis of α -pinene (Bertozzi, 2021). The ice nucleation ability of the coated particles was only measured once, at the end of the coating procedure, by means of an AIDA expansion run started at 228 K (see Section 3.4). At that time, the instrumentation required to continuously measure the ice nucleation ability by sampling devices such as CFDCs was not yet available. Fig. 4.2 shows the ice nucleation onsets of the bare feldspar particles together with those measured at

the end of the coating procedure (the SOM coating was only done with the FS04 particles). While the ice nucleation onsets (corresponding to $AF = 0.1\%$) for the bare FS01 and FS04 particles are at very low values in the range $S_{ice} = 1.1 - 1.2$, coating shifts the onset conditions to higher humidity values near the homogeneous freezing line for aqueous solution droplets. Although the coating thickness could not be determined exactly, it was assumed to be rather small because the coating procedure did not result in a measurable increase in the diameter of the dust mode in the size distribution measurements. It was concluded that the small amount of coating mass (either liquid sulfuric acid or highly viscous SOM) was sufficient to block the ice-active sites on the mineral surface (Bertozzi, 2021).

4.1.4 Motivation for a new set of coating experiments

The coating experiments conducted during the Fifth Ice Nucleation Workshop – part 1 were a first step towards a realistic simulation of the processing of dust particles reaching the free and upper troposphere: The coating was applied in situ at a low temperature and comprised only a thin layer of coating material. This was intended to mimic the signal strength of the single-particle mass spectra that are typically observed during field measurements. This was intended to reproduce the intensities of coating-associated peaks typically observed in single-particle mass spectra during airborne measurements. (Shen et al., 2024a). However, as is evident from the discussion in Section 4.1.2 and Section 4.1.3, previous experiments only covered a small proportion of the range of coating types expected in the atmosphere. Furthermore, due to advances in instrumentation, CFDCs are now routinely used for accurate ice nucleation measurements under cirrus conditions.

This thesis presents the results of an extended set of low-temperature coating experiments conducted with K-feldspar particles at the AIDA facility. The AIDA chamber was hereby only used as the reaction or processing tank, while the change in the ice nucleation ability of the dust particles was continuously measured by the CFDC, mINKA (Section 3.3). While also repeating the previous sulfuric acid coating experiment to check consistency with the earlier measurements, for the first time, the ice nucleation ability of nitric acid-coated dust particles was investigated under cirrus conditions. Previous measurements were limited to a temperature range of 248 K to 238 K (Kulkarni et al., 2015). Regarding SOM coating, in view of the recent studies underlining the atmospheric significance of isoprene in the upper troposphere, the type of precursor was changed from α -pinene to isoprene. A “double-coating” experiment was also conducted, involving consecutive nitric acid and SOM coatings.

Another research objective was to change liquid acidic coatings in situ to ammonium salt coatings by adding ammonia to the AIDA chamber (Cziczo et al., 2009). Such experiments were conducted for both the nitrate and sulfate systems, and, as already indicated in Section 4.1.2, could lead to the formation of crystalline coating layers of ammonium nitrate and ammonium

sulfate, respectively. It is important to emphasize here the difference to the procedure of the ammonium sulfate-coating experiment from Eastwood et al. (2009). In that study, the coating layer was forced to crystallize by the initial conditioning step at room temperature and low RH. In the present experiments, the AIDA chamber was maintained at 223 K and S_{ice} about 0.97 throughout the coating process. These humidity conditions are above the homogeneous efflorescence point of ammonium sulfate (Cziczo et al., 1999). As mentioned previously, the homogeneous efflorescence of ammonium nitrate solution droplets is completely prevented. Therefore, crystallization in the AIDA experiments can only occur heterogeneously with the aid of a foreign substance, that is, the feldspar mineral surface.

If crystallization of the coating layer occurred, a significant effect on the particles' ice nucleation ability could be expected. Similar to crystalline ammonium sulfate, also solid ammonium nitrate particles were found to be efficient INPs under cirrus conditions (Wagner et al., 2020; Wang et al., 2022). This could result in a “cyclic” ice nucleation behavior: the bare feldspar particles would initially show a heterogeneous ice nucleation mode, which could be masked or suppressed by the acidic liquid coating. Neutralization by ammonia could then “restore” the particles' heterogeneous ice nucleation ability, but it would now be due to the ice-active sites of the crystalline coating material.

4.2 Aerosol injection and experimental protocol for simulated atmospheric aging

The coating experiments followed a standard sequence: (i) injection of the dust aerosol particles (K-feldspar and Asian dust) into the cleaned, temperature-controlled AIDA chamber; (ii) characterization of the bare dust particles through number concentration and size distribution measurements, single-particle mass spectrometric measurements with Particle Analysis by Laser Mass Spectrometry-Next Generation (PALMS-NG) to infer the chemical composition, and ice nucleation measurements with mINKA; (iii) stepwise addition of aging precursors as described below, while continuously monitoring the evolution of the particle properties detailed in step (ii), but now for the coated particles; and (iv) a final AIDA expansion to probe the particles' ice nucleation ability under dynamically increasing ice supersaturation after completed coating directly in the AIDA chamber, as a comparative benchmark for the extractive mINKA measurements.

The AIDA chamber was maintained at 223 K and near ice-saturated conditions ($S_{ice} = 0.97$), as controlled by an ice coating on the inner chamber walls (see Chapter 3). The ice nucleation measurements with mINKA were conducted at the same temperature of 223 K.

Batches of the feldspar samples FS01 and FS04 used previously were no longer available, and instead, the sample labeled FS02 was used. The sample labels, together with their source

Table 4.1: Mineral composition and source of the feldspar samples used for the present ice nucleation experiments (FS02) and those conducted during the Fifth Ice Nucleation Workshop - part 1 (FS01 and FS04), adopted from Peckhaus et al. (2016); see also Table 8.1, Bertozzi (2021).

Sample	Source	Mineral composition (XRD)
FS01	Minas Gerais, Brazil, supplied by IAG TU Darmstadt	76 % K-feldspar (microcline); 24 % Na/Ca-feldspar (albite)
FS02	Bureau of Analyzed Samples, UK, standard BCS 376	80 % K-feldspar*; 16 % Na/Ca-feldspar*; 4 % quartz
FS04	Mt. Maloso area (Malawi), supplied by IAG TU Darmstadt	80 % K-feldspar (microcline); 18 % Na/Ca-feldspar (albite); 2 % quartz

* Mineral phase was not specified.

and mineral composition, are summarized in Table 4.1. As all batches are dominated by K-feldspar, the notation “K-feldspar particles” can be used for simplicity.

The Asian dust batch (label AD03) is a surface dust sample from the Taklamakan Desert and was collected on 14 January 2022 at Lop County, Hotan Prefecture (37.5177° N, 80.4413° E, Hu, 2026).

The FS02 and AD03 powder samples (sieved fractions, $< 20 \mu\text{m}$) were dispersed and injected into the AIDA chamber using a rotating brush generator (RBG 1000, Palas GmbH) operated with dry, particle-free synthetic carrier gas. The aerosol flow was passed through two cyclone impactors (stages 2 & 3) to limit the particle size distribution to diameters below $5 \mu\text{m}$. To combine the SMPS and APS size distribution measurements, the mobility and the aerodynamic diameters were converted to volume-equivalent diameters. For the K-feldspar particles, a dynamic shape factor of 1.0 and a density of 2.56 g cm^{-3} were used for this conversion (see Section 3.1.3). The same parameters were used for the coated particles, because the thin coating layer did not notably alter the feldspar mode, which was centered at about $0.21 \mu\text{m}$. A density of 2.6 g cm^{-3} was used in the case of experiments with the AD03 sample (Park et al., 2003). Exemplary size distribution measurements are discussed in detail in Section 4.4 and Section 4.5. The number concentration of pre-added dust aerosol particles was typically in the range from 650 cm^{-3} to 750 cm^{-3} .

The gaseous precursors and oxidants required to achieve the various types of coatings are given below. Detailed mixing ratios of the reactants are given in Section 4.4 and Section 4.5. Here, only the basic oxidation conditions are summarized.

Nitric acid coating: The nitric acid coating was achieved by the oxidation of NO_2 with two different oxidants. In the first experiment, NO_2 was oxidized by hydroxyl radicals OH,

generated from the dark ozonolysis of tetramethylethylene (TME), (C_6H_{12}), to produce nitric acid that could condense on the pre-added dust particles. In the second experiment, NO_2 was oxidized by O_3 only, yielding N_2O_5 . N_2O_5 could then hydrolyze in surface-adsorbed water on the dust particles to yield the nitric acid coating. The results from these experiments are described in Section 4.4.1.

Sulfuric acid coating: The sulfuric acid coating was achieved by the oxidation of SO_2 with hydroxyl radicals, generated from the dark ozonolysis of TME, to produce sulfuric acid that could condense on the pre-added dust particles. The results from this experiment are described in Section 4.4.2.

Isoprene-derived SOM coating: The SOM coating material was produced from the oxidation of isoprene by hydroxyl radicals, generated from the dark ozonolysis of TME. The results from this experiment are described in Section 4.4.3.

Double coating of nitric acid and SOM: The initial nitric acid coating was achieved by the $NO_2 + O_3$ oxidation pathway. With an excess of ozone still present, isoprene and TME were added to generate condensable SOM from the oxidation of isoprene by hydroxyl radicals. The results from this experiment are described in Section 4.4.4.

Ammonium nitrate coating: The initial nitric acid coating was achieved here by the oxidation of NO_2 with hydroxyl radicals. Afterwards, ammonia (NH_3) was added in excess to neutralize the acidic coating layer. The results from this experiment are described in Section 4.5.1.

Ammonium sulfate coating: The initial sulfuric acid coating was achieved by the oxidation of SO_2 with hydroxyl radicals. Afterwards, NH_3 was added in excess to neutralize the acidic coating layer. The results from this experiment are described in Section 4.5.2.

Ozone was produced with a silent discharge generator (Semozon 030.2, Sorbios) from pure oxygen. The other precursor gases were provided in gas bottles with 1000 ppm NO_2 in N_2 , 1 % SO_2 in N_2 , 2 % NH_3 in N_2 , and 1 % TME in N_2 . Isoprene was added by evaporating the requested amount of the substance into a 1-liter glass bulb, which was then flushed with dry synthetic air and transferred to the AIDA chamber.

The following chapters provide a detailed description of the ice nucleation measurements of bare and coated dust particles. The text focuses on the feldspar experiments with the FS02 sample. Occasionally, reference is made to complementary experiments with AD03, whose data are included in the appendix. Furthermore, the main focus is on the continuous ice nucleation measurements obtained with mINKA. Therefore, the result from the single AIDA expansion run conducted at the end of the coating procedure is not addressed explicitly.

4.3 Ice nucleation activity of the bare K-feldspar particles at cirrus conditions

The ice nucleation onsets, inferred from all mINKA humidity scans with the bare K-feldspar particles of type FS02, are shown as the blue squares in Fig. 4.3. They correspond to an ice-active aerosol particle number fraction of 0.1 %. Most measurements were conducted at 223 K, i.e., the temperature at which also the continuous ice nucleation measurements during the coating process were conducted. However, a couple of scans were also conducted at lower and higher temperatures.

The FS02 particles clearly induce heterogeneous ice nucleation below homogeneous freezing conditions, but they do not show the particularly low ice nucleation onsets inferred from the previous measurements with the particles from the FS01 and FS04 batches (green and yellow triangles in Fig. 4.3). Comprehensive ice nucleation measurements at mixed-phase cloud conditions have already shown that there is strong variability in the ice nucleation ability even within the feldspar group of minerals (Harrison et al., 2016). This is explained by variations in the elemental composition, morphology, and available active sites on the particles. The ice nucleation ability of the FS02 particles is in better agreement with the orthoclase-type particles investigated by Yakobi-Hancock et al. (2013) (red circle in Fig. 4.3).

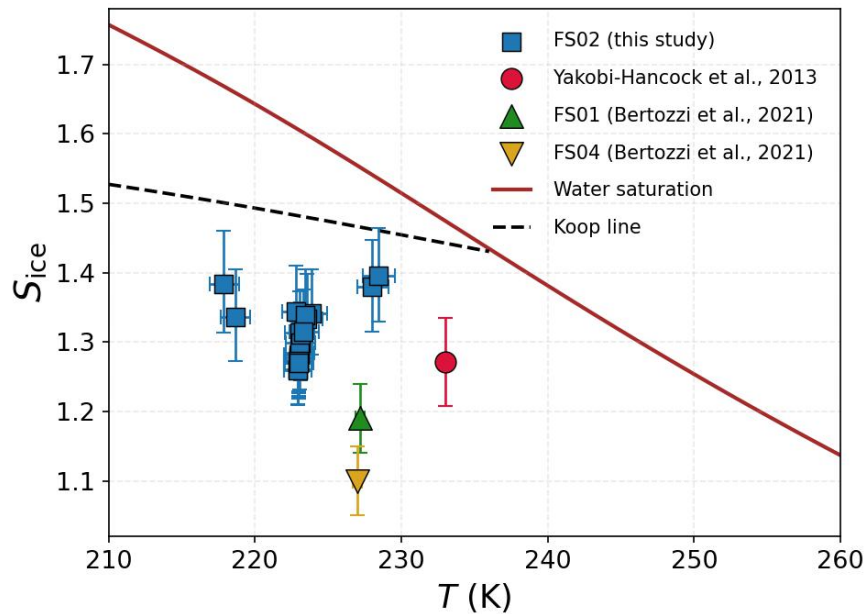


Figure 4.3: Ice nucleation onset conditions ($AF = 0.1\%$) for various types of K-feldspar particles at cirrus temperatures. Blue squares show the critical ice saturation ratios inferred from the mINKA measurements with the FS02 sample from this study. The green and yellow triangles show the ice nucleation onsets of the K-feldspar samples FS01 and FS04 from previous AIDA expansion experiments (see Figs. 8.2 and 8.3 in Bertozzi, 2021). The red circle represents the onset for 200 nm-sized orthoclase (K-feldspar) particles reported by Yakobi-Hancock et al. (2013).

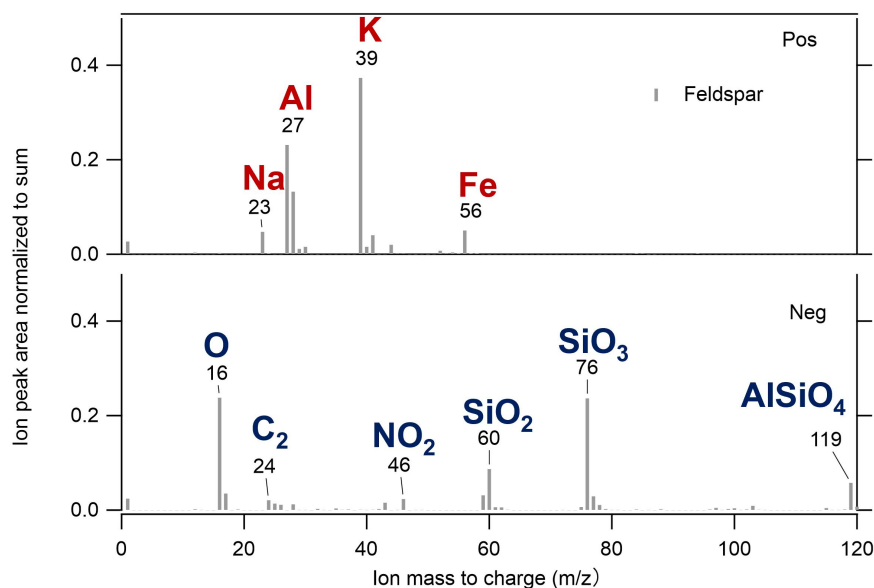


Figure 4.4: Average bipolar mass spectra of the FS02 K-feldspar particles derived from PALMS-NG measurements.

Fig. 4.4 shows the averaged, bipolar mass spectral signals of the FS02 particles from the PALMS-NG measurements. In agreement with the discussion by Shen et al. (2024a), typical cation markers for K-feldspar are at m/z 23 Na^+ , 27 Al^+ , 39/41 K^+ , and 56 Fe^+ , whereas dominant anion markers are at m/z 60 SiO_2^- , 76 SiO_3^- , and 119 AlSiO_4^- .

4.4 Coating of K-feldspar particles with acidic liquids and highly viscous organic matter

4.4.1 The K-feldspar-nitric acid system

The top part of Fig. 4.5 shows the time series of mINKA measurements during the nitric acid-coating experiment, in which NO_2 was oxidized by means of in situ generated hydroxyl radicals. The ice nucleation data are represented as trajectories showing the increase in S_{ice} during the humidity ramps. The color coding denotes the number fraction of ice-active aerosol particles at a given supersaturation. The red diamonds superimposed on the trajectories denote an activated fraction of 0.1 %.

The first scan was done with the bare FS02 feldspar particles and exhibits their intrinsic heterogeneous ice nucleation ability. The coating process was then initiated by the addition of batches of O_3 (1045 ppb, 12:14:30 local time) and NO_2 (104 ppb, 12:19:30 local time). To sustain a continuous production of hydroxyl radicals for the oxidation of NO_2 , TME was then added for a period of 16 min and 20 s (12:23:40 to 12:40:00 local time) with a rate of $5.95 \text{ ppb min}^{-1}$. Already the first mINKA scan conducted after the stop of the TME

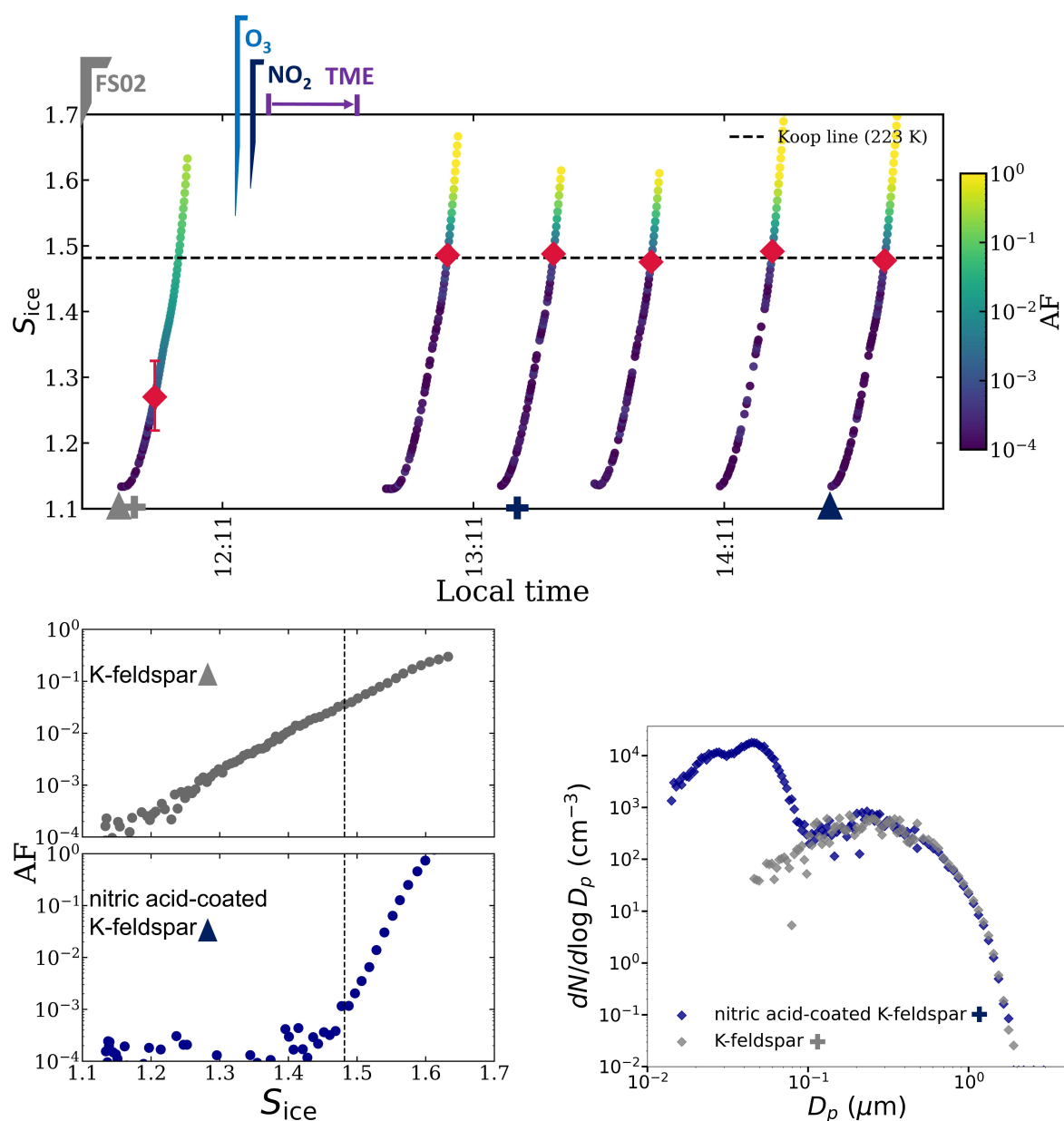


Figure 4.5: Overview of the nitric acid-coating experiment with hydroxyl radicals as the oxidant for NO_2 . Top part: Trajectories of the ice nucleation measurements with mINKA throughout the coating process, using color coding to denote the ice-active fraction of the sampled aerosol particles (see text for details). The black dashed line indicates homogeneous freezing conditions at 223 K (Koop et al., 2000). Red diamonds indicate an activated fraction of 0.1 %. Colored triangles and plus signs on the time axis indicate when the mINKA scans and size distribution measurements, shown in the bottom-left and bottom-right parts, respectively, were performed. The addition of trace gases is symbolized at the top. Bottom left part: ice-active fractions (AF) as a function of ice saturation ratio from mINKA scans with the bare K-feldspar particles (panel (a), gray) and nitric acid-coated K-feldspar particles (panel (b), blue). Bottom right part: combined SMPS-APS size distribution measurements of the bare (gray) and nitric acid-coated (blue) dust particles.

flow showed a dramatic change in the particles' ice nucleation ability. The heterogeneous ice nucleation mode was completely suppressed and the nucleation onset was shifted to homogeneous freezing conditions. A couple of further mINKA scans were conducted to check the consistency of this result, and the ice nucleation behavior indeed remained unchanged. The passivation of the K-feldspar particle surface for ice nucleation under cirrus conditions is similar to that observed at 248 K to 238 K, where a nitric acid coating blocked the depositional ice activity of some dust types (Kulkarni et al., 2015).

The strong suppression of the intrinsic heterogeneous ice nucleation ability of the feldspar particles by the nitric acid-coating can also be seen in the different representation style chosen for the graphs in the bottom left part of Fig. 4.5. Instead of the color-coding, the ice-active fractions of the sampled aerosol particles are plotted here directly as a function of the ice saturation ratio during the mINKA humidity ramps, for the bare feldspar particles in panel (a) and for the nitric acid-coated particles in panel (b) (the latter started at 14:36:00 local time).

A noteworthy feature of the OH-initiated coating experiment is that the generated HNO_3 not only condensed on the feldspar particles, but also led to the nucleation of a new particle mode of < 100 nm-sized, pure nitric acid solution droplets. This nucleation mode can be seen in the representative size distribution measurement taken after the stop of the TME flow (blue spectrum in the bottom right part of Fig. 4.5). As these pure solution droplets will only freeze homogeneously, the ice-active fractions of the particles sampled by mINKA after coating were not normalized to the total aerosol particle number concentration including the nucleation mode, but to the number concentration of the feldspar particle mode only. The separation between the two modes was achieved by a bimodal lognormal fit to the recorded size distributions.

Another important observation from the size distribution measurements is that the size of the bare feldspar particles (gray spectrum) did not increase after coating (blue spectrum). The coating was clearly very thin, but it was not possible to quantify this further. When arguing that PCF might be the dominant heterogeneous ice nucleation pathway, it is indeed possible that a small coating mass could fill all relevant pores or cracks with a solute, thereby impeding the condensation and freezing of pure supercooled water. In any case, the liquid coating has eliminated any traces of the feldspar particles' intrinsic ice nucleation ability and now determines the ice nucleation behavior on its own, leading to homogeneous freezing conditions.

As a final note regarding this first aging experiment, the reaction of TME with ozone not only produced OH radicals but also acetone, $\text{C}_3\text{H}_6\text{O}$, and oxygen. The acetone formed in the reaction likely remained predominantly in the gas phase because of its comparatively low reactivity, although signals attributable to condensed-phase acetone were also observed in the PALMS-NG spectra (not shown here). For simplicity, the term "nitric acid" coating was

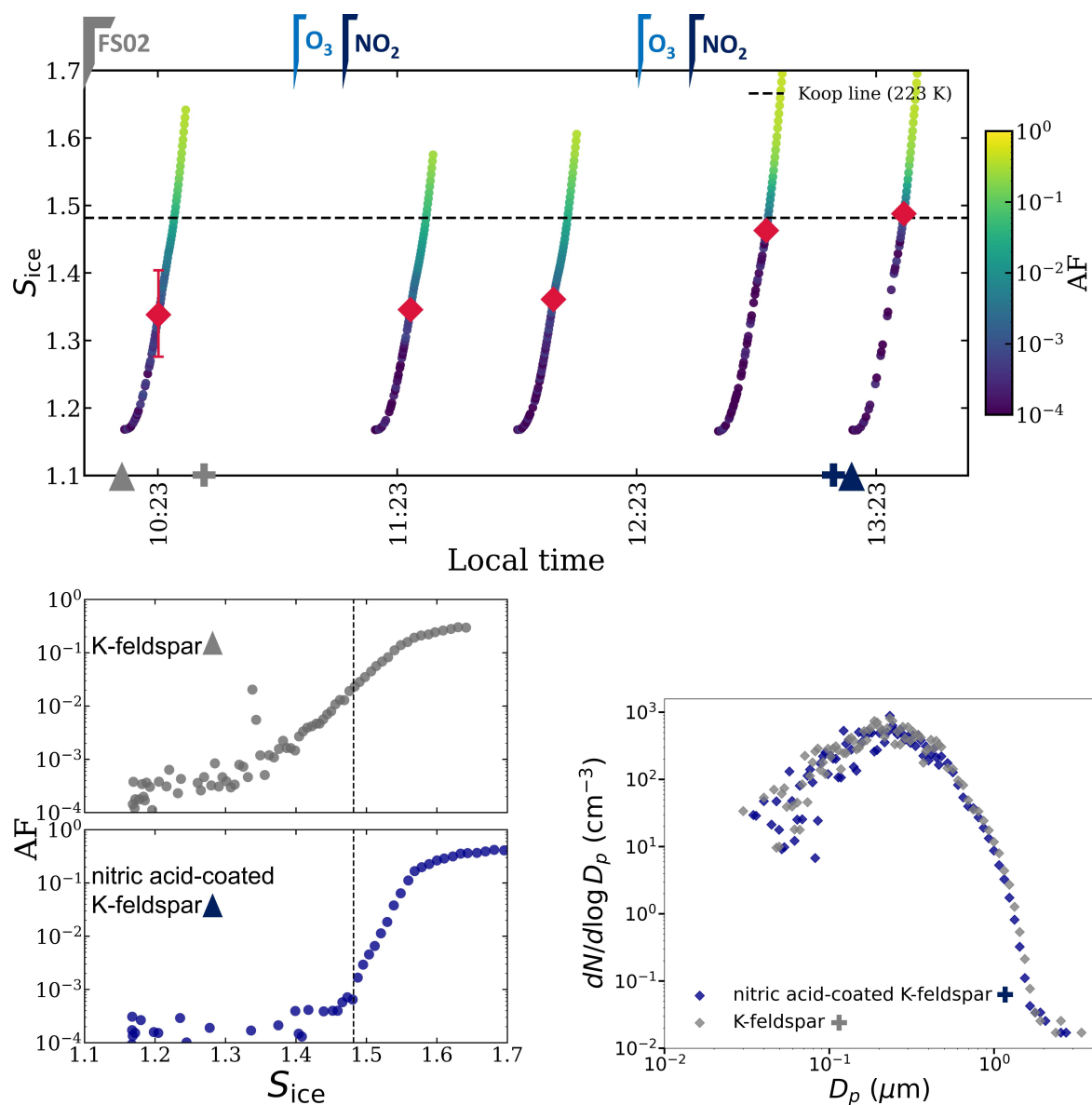


Figure 4.6: Overview of the nitric acid-coating experiment with the $\text{NO}_2 + \text{O}_3$ oxidation pathway. Top part: Trajectories of the ice nucleation measurements with mINKA throughout the coating process, using color coding to denote the ice-active fraction of the sampled aerosol particles (see text for details). The black dashed line indicates homogeneous freezing conditions at 223 K (Koop et al., 2000). Red diamonds indicate an activated fraction of 0.1 %. Colored triangles and plus signs on the time axis indicate when the mINKA scans and size distribution measurements, shown in the bottom-left and bottom-right parts, respectively, were performed. The addition of trace gases is symbolized at the top. Bottom left part: ice-active fractions as a function of ice saturation ratio from mINKA scans with the bare K-feldspar particles (panel (a), gray) and nitric acid-coated K-feldspar particles (panel (b), blue). Bottom right part: combined SMPS-APS size distribution measurements of the bare (gray) and nitric acid-coated (blue) dust particles.

used in this section, but it may be that the aqueous coating contained traces of organic or acid-dissolved mineral components.

In the second nitric acid-coating experiment, NO_2 was oxidized by O_3 only. The respective measurement data are shown in Fig. 4.6, with an identical arrangement and content of the graphs as in Fig. 4.5. The coating was done here in two steps. In the first step, only a comparably small amount of NO_2 (20 ppb) was added, together with 660 ppb of ozone. This only marginally increased the ice nucleation onset of the pre-added feldspar particles in the mINKA measurements, indicating that there is a critical mass of coating material needed to mask the active sites on the mineral surface. In the second coating step, which took place at around 12:36:00 local time, another batch of NO_2 was added. With a concentration of 103 ppb, this was similar to that used in the OH-induced coating experiment described above. At the same time, the ozone mixing ratio was increased to 5410 ppb. The increase in the precursor concentration led to a similar result as for the first coating experiment: the ice nucleation onset was quickly shifted to homogeneous freezing conditions in the succeeding mINKA humidity scans. The exemplary AF vs. S_{ice} plot of the nitric acid-coated particles in panel (b) of the bottom left graph corresponds to the last mINKA scan, which was started at about 13:17:00.

As a notable difference compared to the first coating experiment, the $\text{NO}_2 + \text{O}_3$ oxidation pathway did not lead to the nucleation of a new particle mode of pure nitric acid solution droplets. Instead, the generated N_2O_5 simply underwent hydrolysis on the dust surface, again without inducing a detectable increase in the diameter of the feldspar particles.

4.4.2 The K-feldspar-sulfuric acid system

The sulfuric acid-coating experiment described in this section aimed to replicate the findings of the previous AIDA experiments with the FS01 and FS04 samples and to prepare the ground for the new coating step involving the neutralization of the acidic liquid layer with ammonia, as described in Section 4.5.2. The measurement data are shown in the common format in Fig. 4.7. As shown by the labels in the top graph, the experiment involved four individual coating steps: ozone was added once at the start of the coating process at 10:56:00 local time (898 ppb). The successive coating steps then involved the pairwise addition of SO_2 and TME, starting at 11:03:00 (3 ppb SO_2 and 5.95 ppb min^{-1} TME for 5 min), at 12:12:00 (3 ppb SO_2 and 5.95 ppb min^{-1} TME for 13 min), at 14:13:00 (6 ppb SO_2 and 11.9 ppb min^{-1} TME for 16 min), and at 16:02:00 (12 ppb SO_2 and 11.9 ppb min^{-1} TME for 14 min). For comparison, the coating experiments with the FS01 and FS04 samples used singular SO_2 precursor additions of about 2.5 and 5 ppb, respectively (Bertozzi, 2021). As shown in Fig. 4.2, those amounts were sufficient to completely suppress the intrinsic heterogeneous ice nucleation ability of the FS01 and FS04 particles. In contrast, the deactivation of the ice nucleation ability of the FS02 particles progressed more slowly. After the first two coating steps, there was barely any

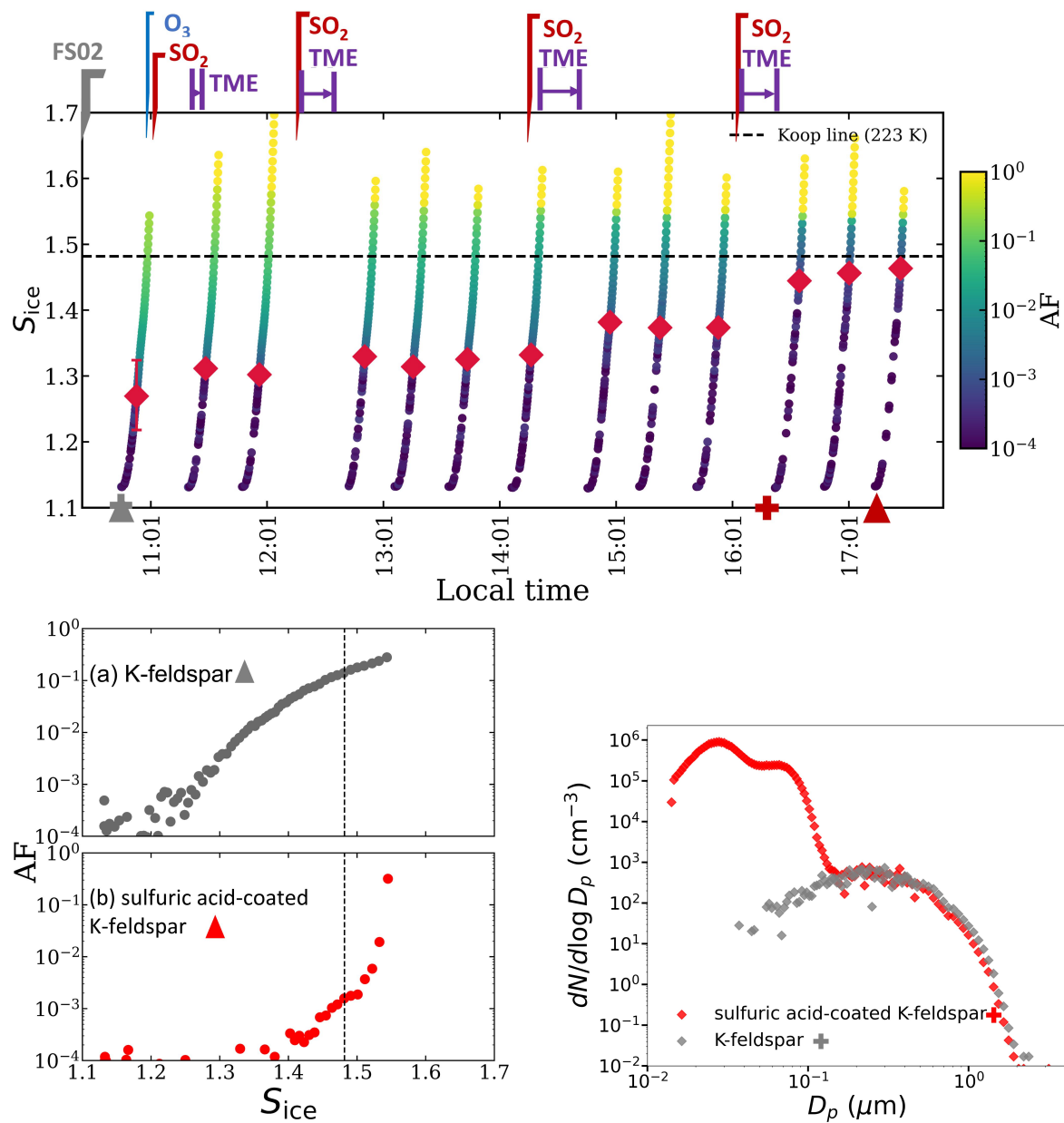


Figure 4.7: Overview of the sulfuric acid-coating experiment with hydroxyl radicals as the oxidant for SO_2 . Top part: Trajectories of the ice nucleation measurements with mINKA throughout the coating process, using color coding to denote the ice-active fraction of the sampled aerosol particles (see text for details). The black dashed line indicates homogeneous freezing conditions at 223 K (Koop et al., 2000). Red diamonds indicate an activated fraction of 0.1 %. Colored triangles and plus signs on the time axis indicate when the mINKA scans and size distribution measurements, shown in the bottom-left and bottom-right parts, respectively, were performed. The addition of trace gases is symbolized at the top. Bottom left part: ice-active fractions as a function of ice saturation ratio from mINKA scans with the bare K-feldspar particles (panel (a), gray) and sulfuric acid-coated K-feldspar particles (panel (b), red). Bottom right part: combined SMPS-APS size distribution measurements of the bare (gray) and sulfuric acid-coated (red) dust particles.

increase in the ice nucleation onset. Only after increasing the SO₂ mixing to 12 ppb in the last coating step, an almost complete deactivation of the feldspar particles could be achieved, meaning that the ice nucleation onset was shifted to homogeneous freezing conditions. The exemplary AF vs. S_{ice} plot of the sulfuric acid-coated particles in panel (b) of the bottom left graph corresponds to the last mINKA scan, which was started at about 17:15:00. Note that the ice-active fractions for the coated particles were again computed in relation to the dust particle number concentration only, i.e., omitting the particles from the nucleation mode of small sulfuric acid solution droplets that also formed during coating (see bottom right part of Fig. 4.7).

The reason for the different behavior of the FS02 particles remains elusive. Key experimental parameters such as temperature, aerosol number concentration, and size were similar between the FS02 and FS01/04 experiments. One might speculate that the mineral surfaces of the FS01 and FS04 particles were chemically more affine towards the uptake of H₂SO₄ than the FS02 particles, meaning that condensation of the generated sulfuric acid on the mineral surface was favored over new particle formation through nucleation together with water molecules (which, however, was also observed in the FS01 and FS04 coating experiments). As an alternative, the FS01 and FS04 particles may have a smaller number of cracks and pores, albeit with high ice activity, which could be blocked by a smaller amount of coating material. In spite of the higher SO₂ precursor concentration needed to mask the intrinsic ice nucleation ability of the FS02 particles, it should be noted that the coating mass was still so small that it did not induce a detectable increase in the diameter of the dust mode in the size distribution measurements (Fig. 4.7, bottom right).

4.4.3 The K-feldspar-isoprene SOM system

This experiment marks the first time that the atmospherically relevant precursor type isoprene has been oxidized to generate SOM that can condense on the pre-added dust particles (Fig. 4.8). For that purpose, batches of O₃ (1005 ppb) and isoprene (IP) (70 ppb) were added at 13:28:00 and 13:32:00 local time, followed by two oxidation periods with hydroxyl radicals, induced by the continuous addition of TME: between 13:39:00 and 13:48:00, and between 14:17:00 and 14:34:00, each with 11.9 ppb min⁻¹.

The first oxidation period already shifted the ice nucleation onset of the (partially) coated FS02 particles close to the homogeneous freezing threshold. The second period, where the reaction time was doubled, led to a further increase in the ice nucleation onset even above that threshold. This can be explained by the highly viscous nature of the coating material, which may delay homogeneous freezing because a higher RH is needed to liquefy the coating and enable it to freeze (Wagner et al., 2017). The exemplary AF vs. S_{ice} plot of the SOM-coated particles in Fig. 4.8 corresponds to the last mINKA scan, which was started at about 15:08:00.

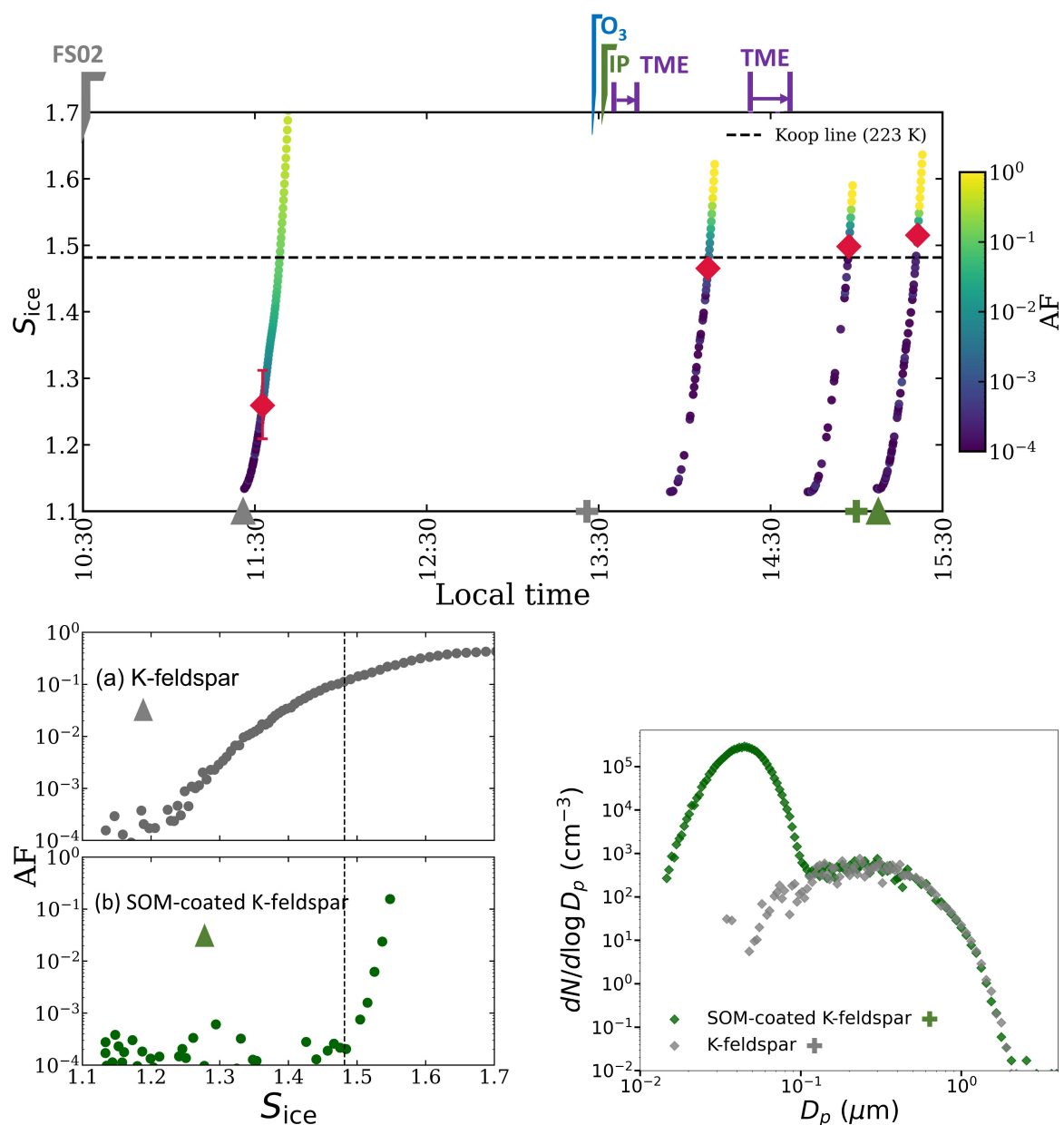


Figure 4.8: Overview of the SOM-coating experiment with hydroxyl radicals as the oxidant for isoprene. Top part: Trajectories of the ice nucleation measurements with mINKA throughout the coating process, using color coding to denote the ice-active fraction of the sampled aerosol particles (see text for details). The black dashed line indicates homogeneous freezing conditions at 223 K (Koop et al., 2000). Red diamonds indicate an activated fraction of 0.1 %. Colored triangles and plus signs on the time axis indicate when the mINKA scans and size distribution measurements, shown in the bottom-left and bottom-right parts, respectively, were performed. The addition of trace gases is symbolized at the top. Bottom left part: ice-active fractions as a function of ice saturation ratio from mINKA scans with the bare K-feldspar particles (panel (a), gray) and SOM-coated K-feldspar particles (panel (b), green). Bottom right part: combined SMPS-APS size distribution measurements of the bare (gray) and SOM-coated (green) dust particles.

Again, the ice-active fractions for the coated particles were computed in relation to the dust particle number concentration only, i.e., omitting the particles from the nucleation mode of pure secondary organic aerosol (SOA) particles that also formed during coating (see bottom right part of Fig. 4.8).

As with the previous experiments involving nitric and sulfuric acid coatings, the SOM coating mass was so small that it did not affect the diameter of the dust particles in the size distribution measurements. Nonetheless, the mass was sufficient to completely dominate the ice nucleation behavior of the particles, masking the ice-active sites on the feldspar surface. This result is in good agreement with the afore-mentioned coating experiments with SOM derived from the oxidation of α -pinene (Koehler et al., 2010; Möhler et al., 2008) and the respective experiment with the FS04 particles conducted during the Fifth Ice Nucleation Workshop – part 1 (see Fig. 4.2). It also agrees with another recent study, where a different INP type, namely crystalline ammonium sulfate, was deactivated by an α -pinene-derived SOM coating (Bertozzi et al., 2021).

4.4.4 Double coating: K-feldspar with nitric acid and isoprene SOM

The double coating was conducted as an initial benchmark experiment for future studies involving more complex scenarios with multiple precursor types. To reduce complexity for this first test, the two coating steps involving nitric acid and isoprene-derived SOM were carried out consecutively, as shown in Fig. 4.9. The initial nitric acid coating was achieved through the oxidation of NO_2 by ozone alone, and was conducted in two oxidation steps, mimicking the procedure described in the context of Fig. 4.6. In the first step, batches of 650 ppb O_3 and 20 ppb NO_2 were added at 10:43:00 and 10:58:00 local time, respectively. The ozone mixing ratio was later increased to 5370 ppb (at 12:32:00), and another, larger batch of 104 ppb NO_2 was added at 13:34:00. In excellent agreement with the experiment described in Section 4.4.1, the oxidation of the first, smaller batch of NO_2 only led to a small deterioration of the intrinsic ice nucleation ability of the pre-added feldspar particles, whereas the later increase in the precursor concentration rapidly shifted the nucleation onset towards homogeneous freezing conditions. An exemplary AF vs. S_{ice} plot of the nitric acid-coated particles from that later time is shown in panel (b) of the bottom left graph.

The next coating step was initiated by the injection of 107 ppb isoprene at 14:48:00, followed by a hydroxyl radical-mediated oxidation period of the organic precursor between 15:11:00 and 15:29:00, where TME was constantly added with a concentration of $11.9 \text{ ppb min}^{-1}$.

The OH-mediated oxidation pathway led to the nucleation of an additional small particle mode of pure SOA particles (Fig. 4.9, bottom right part). The fraction of SOM that condensed on the nitric acid-coated feldspar particles caused the ice nucleation onset to increase further, even beyond homogeneous freezing conditions. As discussed above, this is likely due to

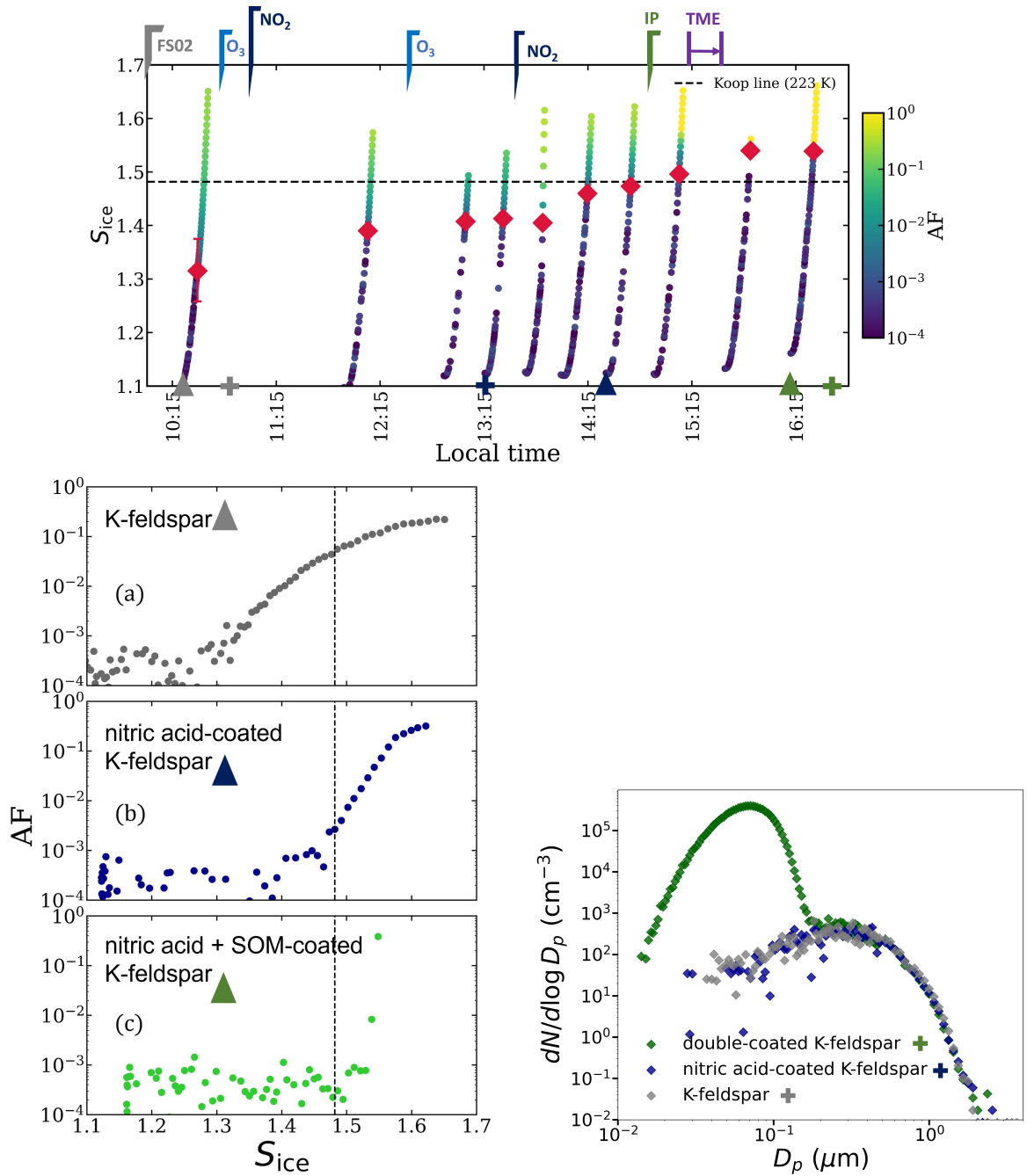


Figure 4.9: Overview of the double-coating experiment with nitric acid and isoprene-derived SOM coatings. Top part: Color-coded ice-active fractions from mINKA humidity scans throughout the coating process. Red diamonds indicate an activated fraction of 0.1 %. Colored triangles and plus signs on the time axis indicate when the mINKA scans and size distribution measurements, shown in the bottom-left and bottom-right parts, respectively, were performed. The addition of trace gases is symbolized at the top. Bottom left part: ice-active fractions as a function of S_{ice} from mINKA scans with the bare K-feldspar particles (panel (a), gray), nitric acid-coated K-feldspar particles (panel (b), blue), and double-coated particles after SOM production (panel (c), green). Bottom right part: combined SMPS-APS size distribution measurements of the bare (gray), nitric acid-coated (blue), and double-coated (green) dust particles.

the increase in viscosity of the coating material. A corresponding AF vs. S_{ice} plot of the double-coated particles is shown in panel (c) of the bottom left graph of Fig. 4.9.

In summary, all coating materials tested in Section 4.4 (i.e., an acidic aqueous solution, highly viscous organic matter, and a combination of the two) ultimately led to the complete suppression of the intrinsic heterogeneous ice nucleation activity of the FS02 K-feldspar particles. The next chapter explores whether and to what extent the heterogeneous ice nucleation capability of the coated particles can be “restored” by transforming the coating layer into a crystalline state.

4.5 Coating of K-feldspar particles with potentially crystalline ammonium salts

4.5.1 The K-feldspar-ammonium nitrate system

The measurement data for the ammonium nitrate-coating experiment are summarized in Fig. 4.10. The experiment is a chronological continuation or extension of the nitric acid-coating experiment discussed in Fig. 4.5, where the OH-mediated oxidation pathway for NO_2 was applied. The first mINKA scan with the bare feldspar particles and the following five scans with the nitric acid-coated particles shown in Fig. 4.10 are essentially the same data as shown in Fig. 4.5. Based on the experience from several test experiments, NH_3 was not added directly after this initial characterization period. Although the fifth mINKA scan for the nitric acid-coated particles still showed a complete deactivation of the intrinsic ice nucleation ability of the feldspar particles, the aqueous nitric acid coating layer may have partially evaporated during the extended characterization phase. Therefore, an additional injection of NO_2 and TME was carried out just before the introduction of ammonia, in order to create a thicker, more persistent nitric acid coating that could be neutralized by ammonia. More accurately, 104 ppb of NO_2 were added at 15:04:00 local time. TME was then added continuously between 15:08:00 and 15:29:00 at a rate of $5.95 \text{ ppb min}^{-1}$. This was immediately followed, at 15:32:00, by the injection of 175 ppb of NH_3 .

The four mINKA scans carried out after the NH_3 addition showed a surprising yet consistent result. The ammonium nitrate-coated feldspar particles again exhibited a distinct heterogeneous ice nucleation mode, with the onset of nucleation occurring roughly between that of the uncoated feldspar particles and the threshold for homogeneous freezing. Although it is not possible to obtain direct evidence of the crystalline phase state of the coating, the only reasonable explanation for this observation is that the neutralized aqueous coating layer has undergone dust-induced efflorescence to form solid ammonium nitrate. The solid coating of ammonium nitrate, which, as already noted above, is a well-known ice nucleating agent at cirrus conditions (Wagner et al., 2020), is then responsible for the observed heterogeneous ice nucleation mode. To assess the efficiency of this heterogeneous ice nucleation mode more

accurately, panel (c) of the bottom left graph in Fig. 4.10 shows a selected activated fraction (AF) vs. S_{ice} plot of the ammonium nitrate-coated particles. Although the heterogeneous ice nucleation mode of the ammonium nitrate-coated particles is clearly obvious, it is about one order of magnitude weaker in terms of the activated fraction than the bare feldspar particles shown in panel (a).

The addition of NH_3 not only neutralized the nitric acid coating on the feldspar particles but also the nucleation mode of pure nitric acid solution droplets formed during the initial NO_2 oxidation by hydroxyl radicals (see discussion of Fig. 4.5). It also led to the formation of another nucleation mode of ammonium nitrate particles. Hence, the particle size distributions measured after ammonia addition are trimodal (Fig. 4.10, bottom right). As discussed above, numerous studies have demonstrated the inhibition of efflorescence in pure ammonium nitrate solution droplets. Nevertheless, an additional blank experiment was conducted to prove that the heterogeneous ice activity observed after the addition of ammonia is indeed related to the feldspar mode (i.e., crystallization of ammonium nitrate is only mediated by the dust surface) and not to the potential crystallization of the pure ammonium nitrate solution droplets. The blank experiment followed the same procedure as shown in Fig. 4.10, with the same precursor concentrations being used. The only difference was that the seed aerosol particles were not introduced. The recorded mINKA scans are depicted in Fig. 4.11.

In detail, a single batch of 1019 ppb O_3 was added at 09:45:00 local time. With the addition of 104 ppb NO_2 and a sustained production of hydroxyl radicals by a constant flow of $5.95 \text{ ppb min}^{-1}$ TME between 09:54:00 and 10:11:00, a nucleation mode of pure nitric acid solution droplets with a medium diameter of about $0.025 \mu\text{m}$ was formed (data not shown). The three mINKA scans of the nitric acid solution droplets showed very high ice nucleation onsets, apparently even above homogeneous freezing conditions. This may be due to the Kelvin effect: for very small droplets, a higher ambient RH is required to reach the critical dilution of the solution and cause it to freeze. Following the initial three mINKA scans, the second NO_2 and TME injection was carried out immediately prior to the introduction of ammonia, as in Fig. 4.10: 104 ppb of NO_2 were added at 11:35:00 local time. TME was added continuously between 11:39:00 and 11:59:00 at a rate of $5.95 \text{ ppb min}^{-1}$. This was immediately followed, at 12:02:00, by the injection of 175 ppb of NH_3 . The mINKA measurements show that the ice nucleation onsets remained well above the homogeneous freezing threshold even after the introduction of NH_3 , demonstrating that the ammonium nitrate particles remained in the liquid state and did not crystallize homogeneously under the AIDA conditions.

Returning to the discussion of the feldspar coating experiment shown in Fig. 4.10, the mass of the ammonium nitrate coating could not be quantified from the single-particle mass spectrometric measurements with PALMS-NG due to pending calibration experiments.

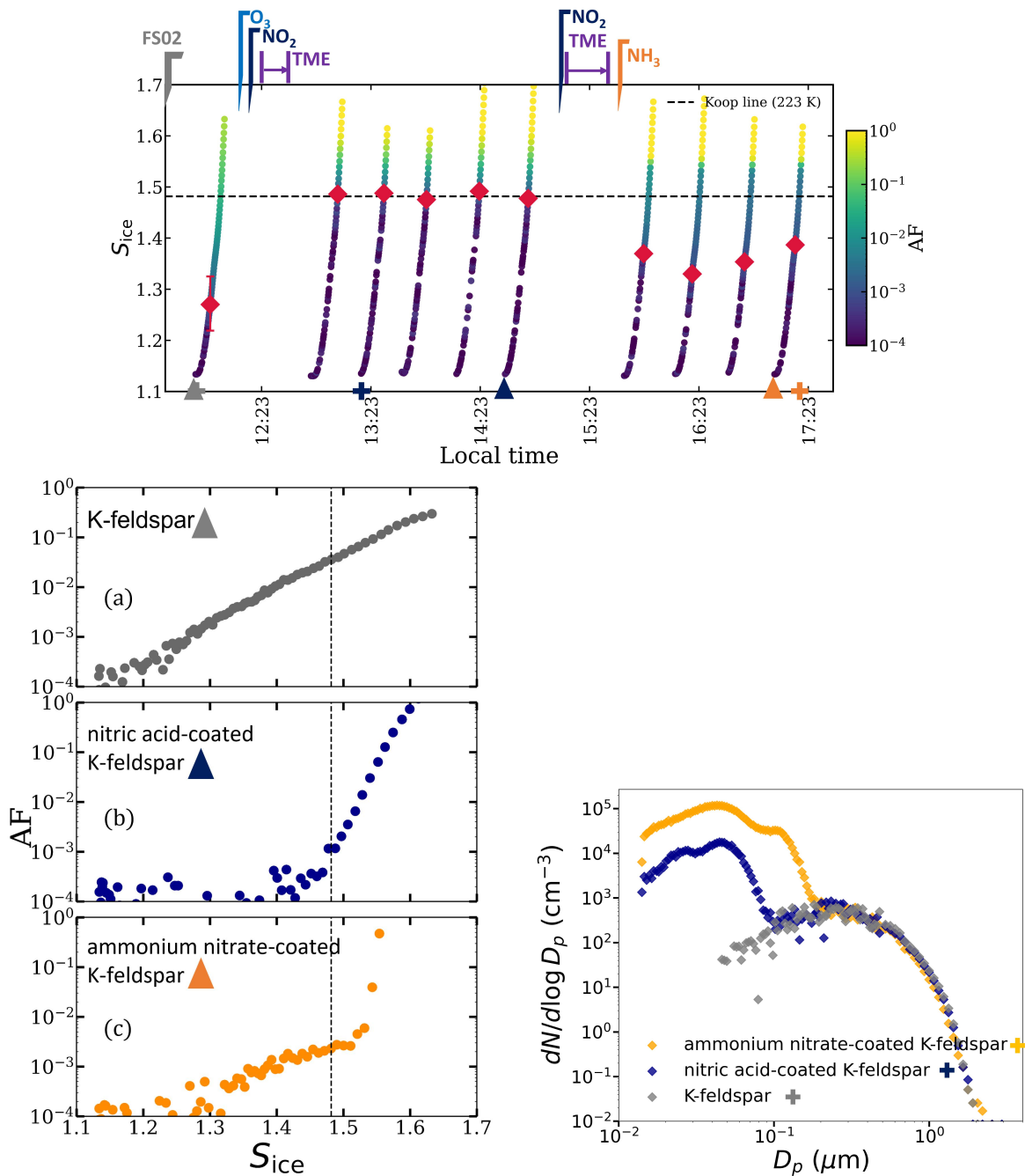


Figure 4.10: Overview of the coating experiment where the aqueous nitric acid coating was neutralized by ammonia. Top part: Color-coded ice-active fractions from mINKA humidity scans throughout the coating process. Red diamonds indicate an activated fraction of 0.1 %. Colored triangles and plus signs on the time axis indicate when the mINKA scans and size distribution measurements, shown in the bottom-left and bottom-right parts, respectively, were performed. The addition of trace gases is symbolized at the top. Bottom left: ice-active fractions as a function of ice saturation ratio from mINKA scans with the bare K-feldspar particles (panel (a), gray), nitric acid-coated K-feldspar particles (panel (b), blue), and ammonium nitrate-coated particles after NH_3 injection (panel (c), orange). Bottom right: combined SMPS-APS size distribution measurements of the bare (gray), nitric acid-coated (blue), and ammonium nitrate-coated (orange) dust particles.

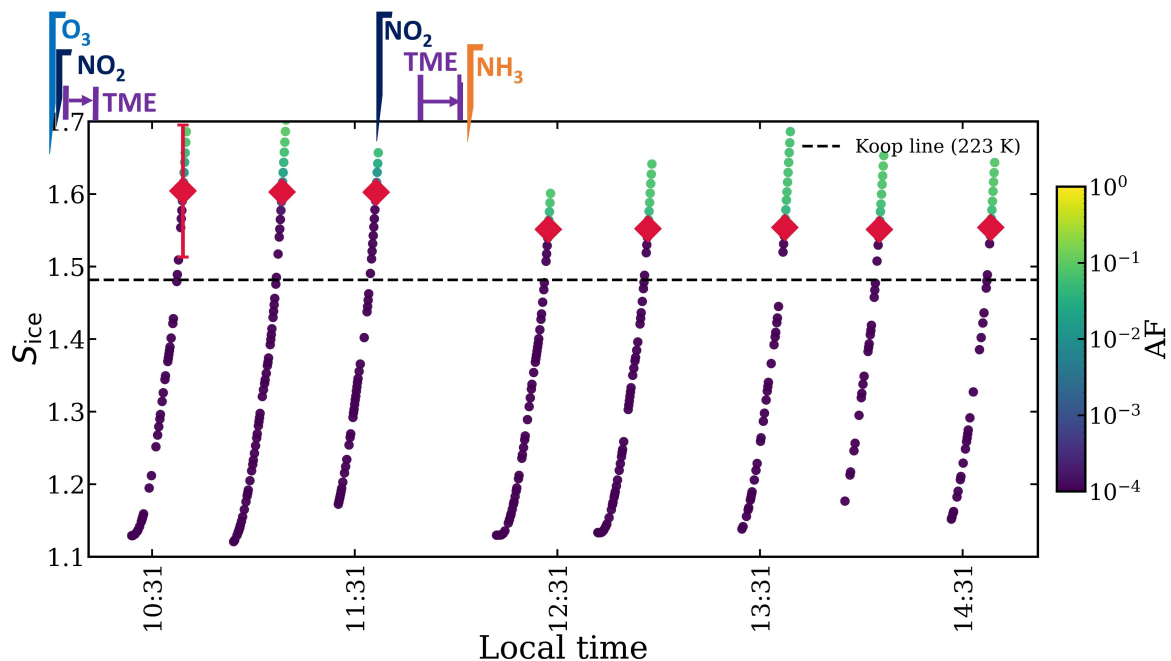


Figure 4.11: Blank experiment with ammonium nitrate particles formed without feldspar seeds. Trajectories of the ice nucleation measurements with mINKA throughout the experiment, using color coding to denote the ice-active fraction of the sampled aerosol particles (see text for details). The black dashed line indicates homogeneous freezing conditions at 223 K (Koop et al., 2000). Red diamonds indicate an activated fraction of 0.1 %. The addition of trace gases is symbolized at the top.

Qualitatively, however, the measurements clearly show that the feldspar particles have been successfully coated with both nitrate and ammonium. Fig. 4.12 shows three representative bipolar mass spectra of individual particles sampled during different periods of the experiment: in the top row a bare feldspar particle, in the central row, a nitric acid-coated particle after the oxidation of NO_2 , and in the bottom an ammonium nitrate-coated particle after the addition of NH_3 .

The single particle spectrum of the bare K-feldspar particle shows the same cation and anion markers as already discussed in the context of the averaged mass spectra shown in Fig. 4.4. Note that the m/z scale of the negative ions was extended in Fig. 4.12, now also showing larger aluminosilicate fragments at e.g., $m/z = 136$ and $m/z = 179$. The presence of a nitric acid coating on the feldspar particles following NO_2 oxidation is evident from the appearance of additional peaks at m/z 46 and 62 in the anion spectrum, which are attributable to NO_2^- and NO_3^- , respectively. After the addition of ammonia, the positive spectrum shows the characteristic peak at m/z 18 for ammonium (NH_4^+). Additionally, the intensity of the NO^+ peak at m/z 30 increases significantly, which is consistent with studies showing that this ion is also formed from ammonium (Murphy et al., 2006).

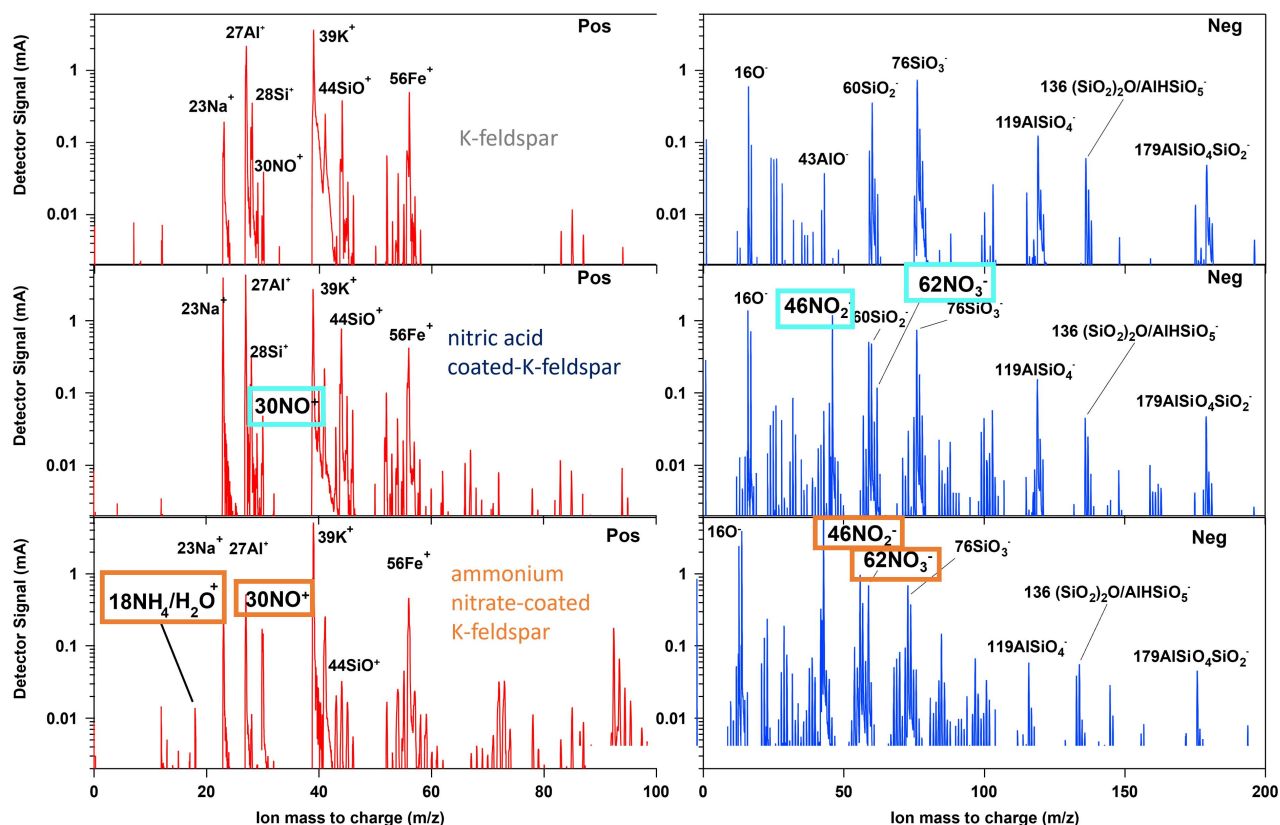


Figure 4.12: Selected bipolar mass spectra of individual particles from PALMS-NG measurements. The three particles were sampled during the ammonium nitrate-coating experiment shown in Fig. 4.10. Top row: bare FS02 K-feldspar particle, central row: nitric acid-coated particle after NO_2 oxidation, bottom row: ammonium nitrate-coated particle after the addition of NH_3 .

A comparative study of the ammonium nitrate coating was also conducted using the AD03 Asian dust sample. The respective measurement data are summarized in Fig. A.1 of the appendix. Although a similar procedure was followed, no enhancement of the particles' heterogeneous ice nucleation ability was observed after the addition of NH_3 . This could indicate that the Asian dust surface was less effective in catalyzing the heterogeneous efflorescence of the ammonium nitrate coating. Due to time constraints caused by the decommissioning of the AIDA chamber, it was not possible to repeat the AD03 coating experiment to consolidate these findings. The directions for future chamber experiments that will help to clarify pending research questions are discussed in more detail in Section 4.6.

4.5.2 The K-feldspar-ammonium sulfate system

The measurement data for the ammonium sulfate-coating experiment are summarized in Fig. 4.13. As with the ammonium nitrate coating, also this experiment is a chronological continuation or extension of a previously discussed experiment, namely the sulfuric acid-

coating experiment shown in Fig. 4.7, where the OH-mediated oxidation pathway for SO₂ was applied. The first mINKA scan with the bare feldspar particles and the following twelve scans with the sulfuric acid-coated particles shown in Fig. 4.13 are essentially the same data as shown in Fig. 4.7. Afterwards, at 17:40:00 local time, 175 ppb of ammonia were introduced to transform the acidic coating into ammonium sulfate. As discussed in Section 4.5.1, the addition of NH₃ neutralized both the sulfuric acid coating on the feldspar particles and the nucleation mode of pure sulfuric acid solution droplets formed during the initial SO₂ oxidation by hydroxyl radicals. Furthermore, it led to the formation of another nucleation mode of ammonium sulfate particles. Hence, the particle size distributions measured after ammonia addition are trimodal (Fig. 4.13, bottom right).

Contrary to the ammonium nitrate-coating experiment shown in Fig. 4.10, the addition of ammonia did not affect the ice nucleation ability of the sulfate-coated particles. The ice nucleation onsets remained at the homogeneous freezing limit. Also, the AF vs. S_{ice} plot of the ammonium sulfate-coated particles shown exemplarily in the bottom left of Fig. 4.13 did not show any trace of a “re-appearing” heterogeneous ice nucleation mode. This is surprising, given that it is well established that crystalline ammonium sulfate exhibits heterogeneous ice nucleation under cirrus conditions (Abbatt et al., 2006; Bertozzi et al., 2021; Bertozzi et al., 2024). It also contrasts with the measurement data for the ammonium sulfate-coated kaolinite particles from Eastwood et al. (2009) (see Section 4.1.3). As mentioned above, Eastwood et al. (2009) pre-conditioned the kaolinite particles at such low RH that homogeneous efflorescence of the ammonium sulfate coating layer was possible. However, under the present AIDA chamber conditions, efflorescence of ammonium sulfate can only occur heterogeneously on the feldspar mineral surface. Therefore, it could be speculated that the K-feldspar surface triggered the crystallization of ammonium nitrate, as described above, but not that of ammonium sulfate. Crystallization of ammonium sulfate was also absent in an earlier experiment using Arizona test dust particles as mineral seeds (Cziczo et al., 2009). As previous contact efflorescence experiments have clearly shown, there can be huge variability in the heterogeneous efflorescence relative humidities for ammonium sulfate and ammonium nitrate solution droplets depending on the type of solid contact nucleus (Davis et al., 2015). These differences are usually explained by the degree to which the crystal structure of the solid nucleus matches that of the potentially crystallizable inorganic compound. Further AIDA experiments involving the coating of different types of dust particles are clearly needed to substantiate this hypothesis.

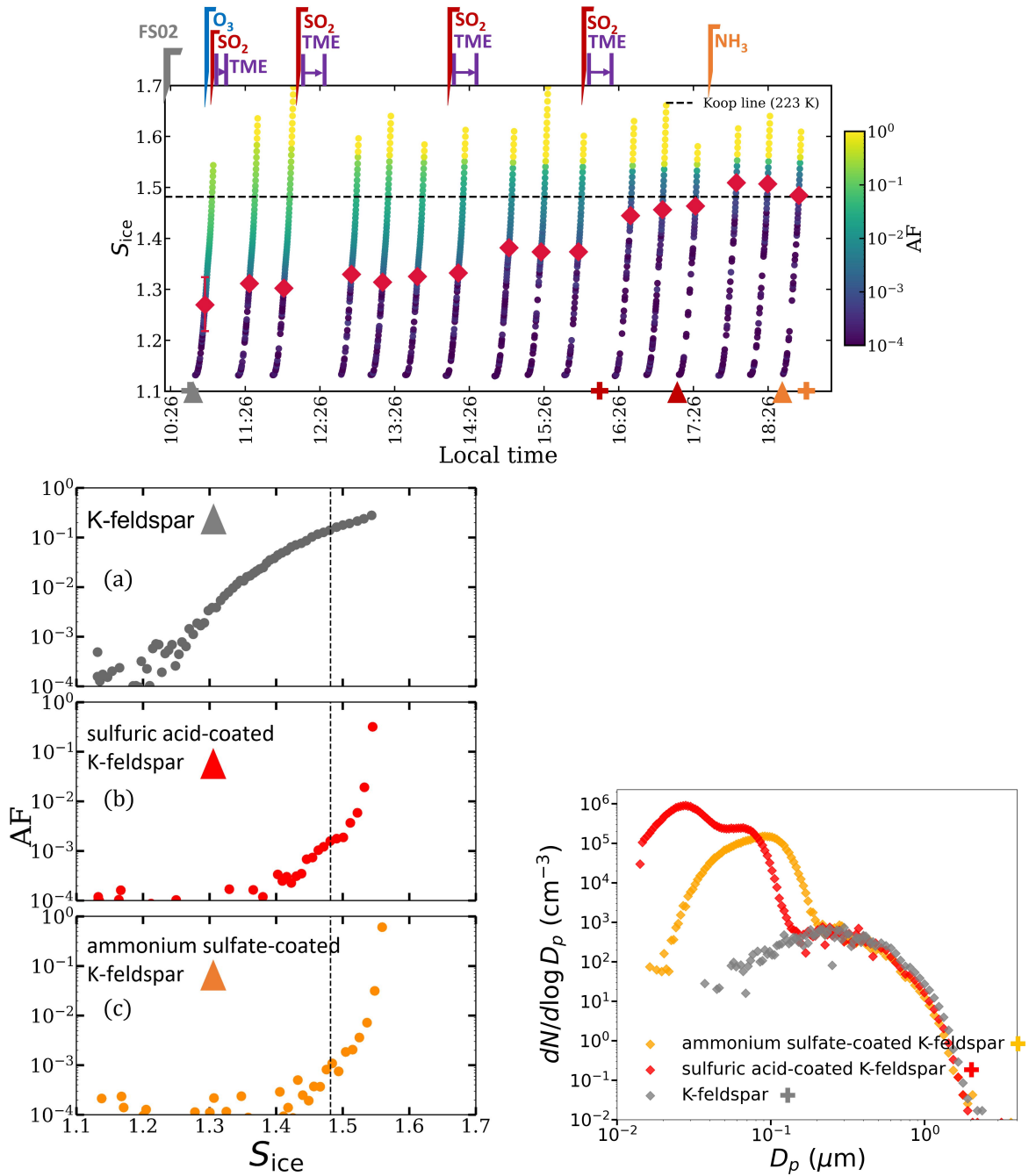


Figure 4.13: Overview of the coating experiment where the aqueous sulfuric acid coating was neutralized by ammonia. Top part: Color-coded ice-active fractions from mINKA humidity scans throughout the coating process. Red diamonds indicate an activated fraction of 0.1 %. Colored triangles and plus signs on the time axis indicate when the mINKA scans and size distribution measurements, shown in the bottom-left and bottom-right parts, respectively, were performed. The addition of trace gases is symbolized at the top. Bottom left part: ice-active fractions as a function of S_{ice} from mINKA scans with the bare K-feldspar particles (panel (a), gray), sulfuric acid-coated K-feldspar particles (panel (b), red), and ammonium sulfate-coated particles after NH_3 injection (panel (c), orange). Bottom right part: combined SMPS-APS size distribution measurements of the bare (gray), sulfuric acid (red), and ammonium sulfate-coated (orange) dust particles.

4.6 Summary and outlook

Dust particles that reach the free and upper troposphere are often processed, which means that they no longer expose their bare mineral surfaces to the environment. This study has produced the most comprehensive database to date of changes in the ice nucleation ability of dust particles coated with substances of atmospheric relevance under cirrus conditions (223 K). K-feldspar particles were used as a proxy for dust. The results for the different types of coating materials discussed in Section 4.4 and Section 4.5 are summarized in Fig. 4.14 in terms of the onset conditions for ice formation.

The overarching result is that all atmospherically relevant coatings lead to a significant suppression of the intrinsic heterogeneous ice nucleation ability of the feldspar particles. For feldspar particles coated with nitric or sulfuric acid, the aqueous layer exerts complete control over the ice nucleation behavior. This results in a shift in the onset conditions towards the homogeneous freezing threshold. For highly viscous SOM coatings, either pure or added on top of a nitric acid coating, a shift even beyond the homogeneous freezing threshold is observed. This might be due to the delayed liquefaction and freezing of the viscous coating material.

Contradicting results are obtained after neutralizing the aqueous nitric and sulfuric acid coating layers with ammonium nitrate and ammonium sulfate, respectively. Neutralization enables the coating layer to transform from a liquid to a solid via heterogeneous efflorescence, which is catalyzed by the mineral surface. However, the measurement data only indicate that this has really happened in the case of ammonium nitrate-coated feldspar particles, as evidenced by heterogeneous ice formation below the homogeneous freezing threshold. Heterogeneous ice formation was absent for ammonium nitrate-coated Asian dust particles (data not included in Fig. 4.14) and ammonium sulfate-coated K-feldspar particles. It was hypothesized that the crystal match between the dust and the inorganic solid controls the RH for heterogeneous efflorescence, and whether this process can happen under AIDA conditions. Clearly, further coating experiments involving a greater variety of dust types are needed to investigate this issue more thoroughly.

Even though the ammonium nitrate-coated feldspar particles exhibited a heterogeneous freezing mode, it should be noted that its efficiency in terms of nucleation onset and activated fraction was significantly lower than that of the feldspar particles alone (see Fig. 4.10). Moreover, the heterogeneous crystallization of the inorganic ammonium nitrate coating layer on the feldspar particles might be impeded when adding a certain mass fraction of viscous organic material (Bodsworth et al., 2010). In that respect, a promising idea for a future series of coating experiments would be to study the oxidation of NO_2 in the presence of increasing amounts of isoprene, concluding with the addition of ammonia. A sufficient mass fraction of

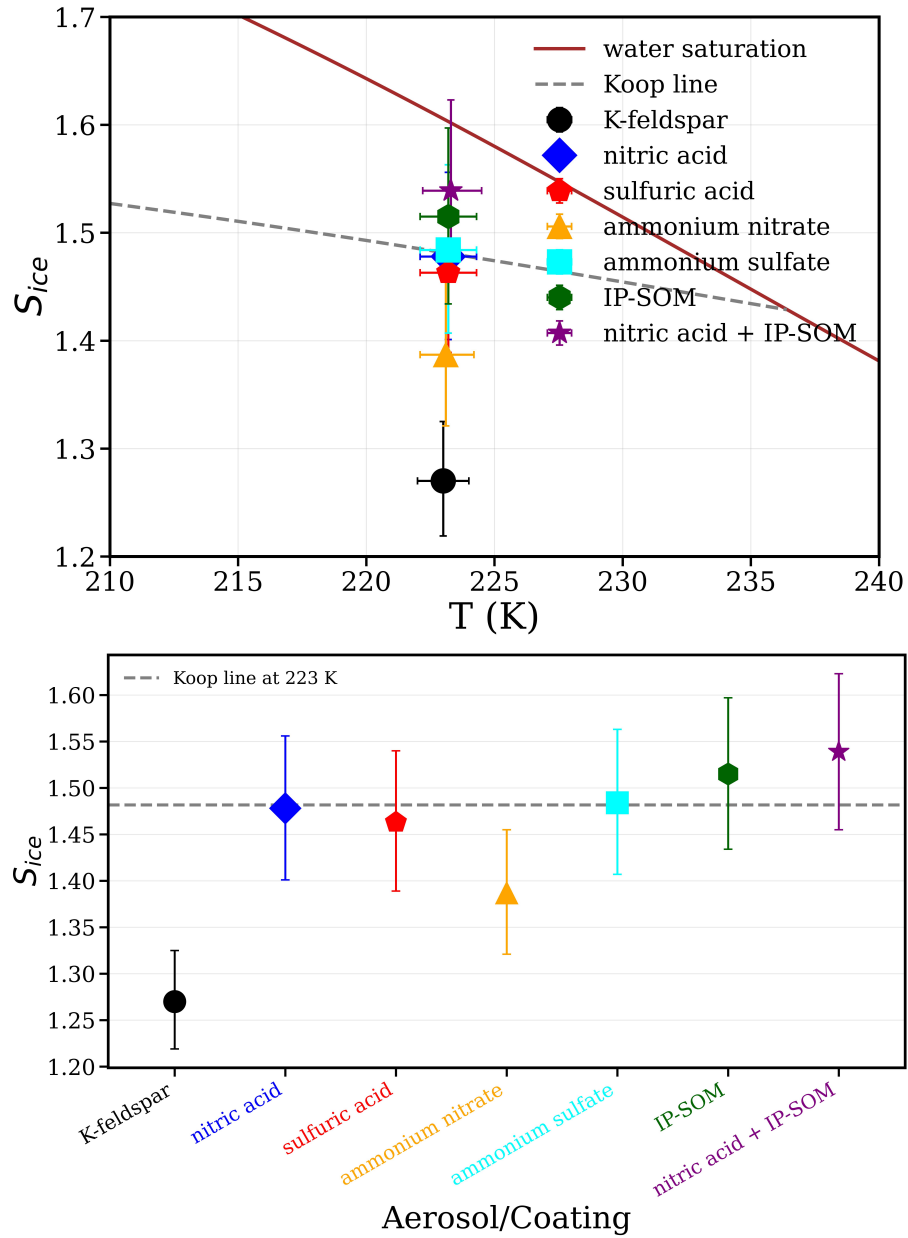


Figure 4.14: Summary of the ice nucleation results from the coating experiments with FS02 K-feldspar particles conducted using different types of precursors. The top panel shows the observed ice nucleation onsets for the bare and coated feldspar particles in the S_{ice} vs. T diagram (onsets for AF = 0.1 %). The lower panel provides a horizontal representation of the same onset conditions (all measured at 223 K) to facilitate comparison between different types of coating.

isoprene-derived SOM could inhibit the crystallization of ammonium nitrate. Alternatively, the co-oxidation of NO_2 and isoprene could lead to a variety of chemical compounds, including organonitrates (Curtius et al., 2024; Mayhew et al., 2023; Rollins et al., 2009), some of which could potentially crystallize. The data in Fig. 4.14 clearly show that cloud models need

to include both “pure dust” and “coated dust” as particle categories in order to accurately predict ice formation under cirrus conditions. However, a stringent parameterization in terms of the coating mass seems problematic because the amount of coating material needed to block the active sites might be highly variable depending on the number and size of pores or crevices that govern the intrinsic heterogeneous ice nucleation ability of the dust. For example, this study found that the FS02 particles apparently required a greater mass of sulfuric acid to become deactivated than the FS01 and FS04 particles in previous AIDA experiments. Some of the ice nucleation experiments presented here were supplemented by single-particle mass spectrometry measurements using PALMS-NG. It is currently planned that a rebuild of this instrument will form part of the standard instrumentation of the AIDA chamber’s successor, Aerosol Interaction and Dynamics in the Atmosphere cold and clean (AIDAc2). This provides an ideal opportunity to “tune” future laboratory-based coating experiments to “realistic” atmospheric conditions, i.e., to replicate the typical signatures of PALMS-NG from airborne measurements in AIDAc2 chamber experiments.

5 Morphological aging of SOA particles through ice cloud-processing

This chapter explores an atmospheric aging pathway in which highly viscous or glassy secondary organic aerosol (SOA) particles can change their surface structure by undergoing cloud processing in a deep convective cloud or a cirrus cloud. Cloud processing can transform the particles' pristine, smooth surface into a porous one, a morphological change that was speculated to increase the heterogeneous ice nucleation ability of the particles under cirrus conditions. The type of aerosol particles investigated here for the first time in this aging process were isoprene-derived SOA particles. The Aerosol Interaction and Dynamics in the Atmosphere (AIDA) cloud chamber was used to realistically simulate the atmospheric cloud-processing cycles and the Continuous Flow Diffusion Chambers (CFDCs), Ice Nucleation instrument of the Karlsruhe Institute of Technology (INKA), and mobile Ice Nucleation instrument of the Karlsruhe Institute of Technology (mINKA) were used to detect potential changes in the particles' ice nucleation ability during aging. Chapter 5 is structured as followed. In Section 5.1, relevant background information is provided on previous ice nucleation measurements with highly viscous or glassy organic aerosol particles, the morphological change that such particles can experience during cloud-processing, and earlier AIDA cloud processing experiments with a different SOA particle precursor, namely α -pinene, which form the basis for the new experiments with isoprene. Section 5.2 describes the generation of the SOA particles. The subsequent central sections, Section 5.3 and Section 5.4, focus on the detailed experimental protocols of the two ice cloud-processing types investigated, deep convective cloud and cirrus cloud processing, respectively, as well as the results of the concomitant ice nucleation measurements using the CFDCs. An overarching discussion of the changes observed upon cloud processing and their atmospheric significance is presented in Section 5.5.

5.1 Background

5.1.1 Glassy organics as INPs under cirrus conditions

Over the past two decades, substantial evidence has emerged suggesting that a wide range of organic aerosol particles can undergo a phase change in the atmosphere. This transformation involves the conversion of low-viscosity aqueous particles, which are prevalent at high relative

humidity (RH) and/or temperature, into highly-viscous semi-solid or glassy solid particles at low RH and/or temperature (Petters et al., 2019; Renbaum-Wolff et al., 2013). A glassy substance is defined as a material with a viscosity greater than 10^{12} Pa s (Angell, 1995). The temperature-dependent viscosity change is a key parameter that influences the kinetics of important atmospheric processes like gas-to-particles partitioning and heterogeneous chemistry (Reid et al., 2018), and is crucial to understand the particles' ice nucleation ability.

While aqueous organic aerosol particles would only freeze homogeneously at high ice saturation ratios under cirrus conditions, the solidified surface of vitrified, glassy particles would open a pathway for heterogeneous ice formation by deposition nucleation or immersion freezing to occur at lower S_{ice} values. This temperature-dependent ice nucleation behavior is schematically shown in Fig. 5.1, based on model simulations for sucrose particles.

The humidification of an initially glassy particle is a gradual process, in which at first the outer particle layers will liquefy, transforming the particle into a mixed solid-liquid state with a solid, glassy core surrounded by an aqueous, liquid shell (partial deliquescence). The transformation into an entirely liquid particle only occurs at higher RHs when the so-called full deliquescence relative humidity (FDRH) is surpassed. The location of the temperature-dependent thresholds for the deliquescence onset and the FDRH in the S_{ice} vs. T diagram (dashed black and thick red lines in Fig. 5.1, respectively) determines the various possible ice nucleation modes. In an atmospheric updraft started at a comparatively high temperature of 229 K (green line), the trajectory already crosses the FDRH at very small ice supersaturations (S_{ice} about 1.05), preventing depositional ice nucleation and yielding ice formation only by homogeneous freezing at S_{ice} above 1.5. In contrast, for the updraft started at a much lower temperature of 213.5 K (crimson red line), the deliquescence onset is shifted to a higher S_{ice} value of about 1.3, increasing the probability that the particles may act as depositional ice-nucleating particles (INPs) before getting partially deliquesced. A third possibility is indicated by the orange trajectory at an intermediate temperature of 221 K, where the particles act as immersion freezing INPs while being in the mixed-phase, partially deliquesced region.

There is ample evidence for heterogeneous ice nucleation on glassy organic aerosol particles, like the pioneering AIDA cloud chamber study, which involved temperature-cycling of citric acid aerosol particles (Murray et al., 2010). The citric acid aerosol particles nucleated ice homogeneously in expansion cooling runs started above 212 K, i.e., in the liquid region of the phase diagram, but nucleated ice heterogeneously at $S_{ice} \approx 1.2$ when cooled below their glass transition temperature. Such measurements were soon extended to other pure organic compounds, like raffinose and levoglucosan (Wilson et al., 2012), sucrose and glucose (Baustian et al., 2012), and are continued until today with a recent study probing the ice nucleation ability of 2-methyltetrols, as a key component of isoprene-epoxydiol-derived SOA (Li et al., 2024). Occurrence of a heterogeneous ice nucleation mode at sufficiently

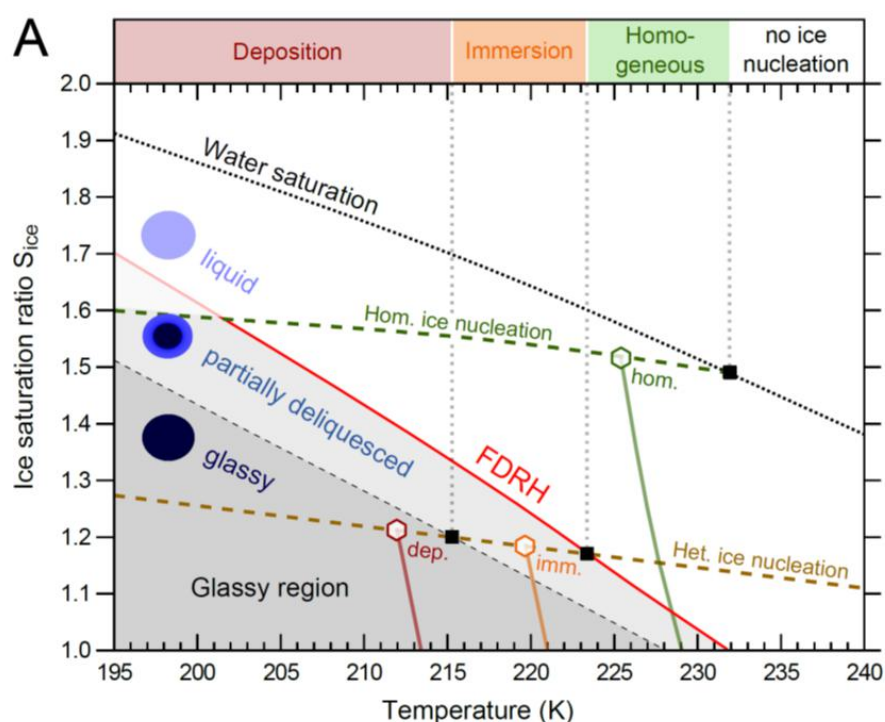


Figure 5.1: Potential ice nucleation modes of glassy organic aerosol particles, exemplified based on simulated updrafts with a $1\% \text{ RH min}^{-1}$ humidification rate for 100 nm-sized sucrose particles (taken from Berkemeier et al. (2014), Fig. 2a therein). Depending on the starting temperature of the three exemplarily shown trajectories, ice nucleation can occur via deposition nucleation (crimson red line), immersion freezing (orange line), or homogeneous freezing (green line).

low temperatures (depending on the type of the compound and its specific glass transition temperature) was a common observation in these studies.

Interestingly, such heterogeneous ice nucleation modes in the glassy regime are rarely observed for “complex” organic aerosol particles, such as SOA particles, which do not consist of a single organic substance but are multicomponent mixtures resulting from complex oxidation reactions followed by gas-to-particle conversion. An important reference in this context is the recent work by Kasparoglu et al. (2022), who have carefully compiled earlier SOA ice nucleation measurements under cirrus conditions, and extended them with new measurements for a variety of precursor molecules, summing up to a database of eleven monoterpene, sesquiterpene, and aromatic precursors of both biogenic and anthropogenic origin. In the vast majority of cases, the ice nucleation onsets of the investigated SOA particles were observed to be at or even above the homogeneous freezing line for aqueous solution droplets in the temperature range between 235 K and 200 K. These results suggest that heterogeneous ice formation by SOA particles is likely uncommon under upper free tropospheric conditions, even at such low temperatures where the particles are most likely in

the glassy state. As a general conclusion, Kasparoglu et al. (2022) therefore recommended to treat glassy or liquid secondary organic material (SOM) and dust coated with glassy or liquid SOM in models as inactive for heterogeneous ice formation. Note that the observed deactivation of the intrinsic heterogeneous ice nucleation ability of the K-feldspar particles by coating them with SOM from the oxidation of isoprene discussed in Section 4.4.3 of this thesis is a further substantiation of this recommendation.

So far, the literature has not discussed why complex SOA particles exhibit a different ice nucleation behavior compared to the single-component organic particles. Tentatively, it might be related to differences in surface chemistry or functionality, like hydroxyl groups to help alignment of ice crystals. Obviously, the vitrified particle surface is more suited to lower the energy barrier for the nucleation of ice in the case of pure sugars or organic acids compared to complex organic mixtures in glassy SOA particles. It must also be noted that there are a few studies that deviate from the general recommendation by Kasparoglu et al. (2022). Wang et al. (2012) and Ignatius et al. (2016) discussed heterogeneous ice nucleation modes for SOA particles derived from naphthalene and α -pinene, respectively. However, the nucleation onsets of the particles in terms of S_{ice} were only slightly (≈ 0.1) below the homogeneous freezing conditions. As a further case, heterogeneous ice formation, however with very low activated fractions of about 10^{-5} , was observed in CFDC measurements for isoprene-derived SOA (Wolf et al., 2020).

The ability of organic aerosol particles to nucleate ice remains a highly active research field, with studies continuing to explore new chemical species such as organosulfates (Rapp et al., 2025). Apart from the type of organic compound or SOA precursor chosen, which may affect surface functionality, there is another process that could be crucial for the particles' ice nucleation ability. This process falls into the general topic of this thesis, namely atmospheric aging processes, and addresses the ice-cloud processing of organic aerosol particles, which can affect surface morphology. This process is introduced in the next section.

5.1.2 Morphological change of glassy organic aerosol particles upon ice-cloud processing

All ice nucleation measurements contained in the compilation by Kasparoglu et al. (2022) were done with pristine SOA particles, partly including pre-cooling to the glassy regime, but without any type of cloud-processing. Typically, as also evidenced by Environmental Scanning Electron Microscope (ESEM) images shown later in this thesis, these pristine SOA particles have a very compact, near-spherical shape with a smooth surface. However, the morphology might change in the course of cloud-processing, either in a deep-convective cloud system, which involves the formation of cloud droplets and ice crystals, or in a cirrus cloud system, where only the formation of ice crystals is involved.

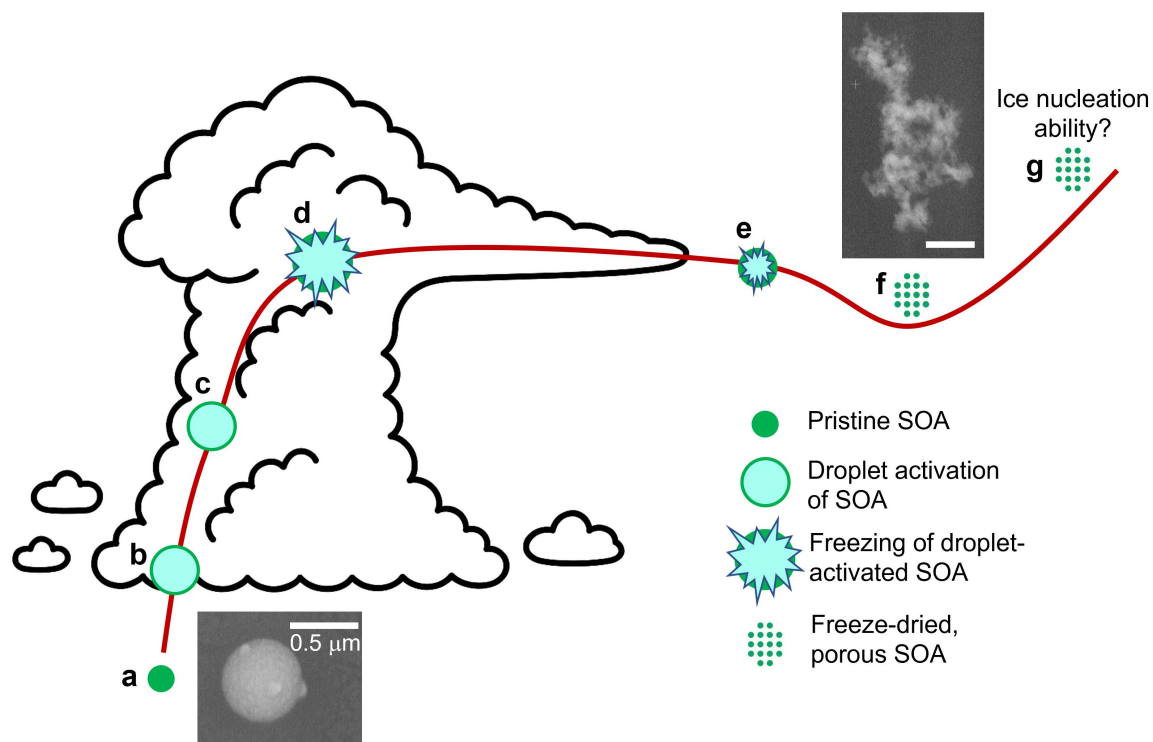


Figure 5.2: Scheme of the atmospheric freeze-drying process proposed by Adler et al. (2013), showing the atmospheric trajectory (red line) of SOA particles that are processed in a deep-convective cloud system. The letters, which annotate key steps in the process, are described in detail in the text. The two ESEM images shown next to steps a and f are recordings from an AIDA cloud chamber experiment, where the atmospheric freeze-drying process was simulated in the laboratory using SOA particles from the ozonolysis of α -pinene (Wagner et al., 2024).

The first type, processing in a deep-convective cloud system, was first studied experimentally by Adler et al. (2013) with organic particles generated from a reference standard, called Suwannee River Natural Organic Matter, using an aerosol flow tube setup. The process, which was also called “atmospheric freeze-drying in ice clouds”, is sketched in Fig. 5.2.

The atmospheric trajectory starts with pristine, compact SOA particles (step a). As an illustration, Fig. 5.2 displays a representative ESEM image of an unprocessed α -pinene-derived SOA particle from an earlier AIDA cloud chamber experiment using the low-temperature particle sampling and transfer technique described in Section 3.2. During the updraft, possibly still at warm temperatures above 273 K, the organic particle will be activated to a cloud droplet when the RH exceeds 100 % (step b). Upon continued updraft, the cloud droplet will supercool (step c) and eventually freeze homogeneously when the temperature drops below about 235 K (step d). Freezing will lead to a phase separation between the ice lattice and a freeze-concentrated organic residual with the potential to vitrify, forming an ice crystal covered with glassy organic material. In drier air with $S_{ice} < 1$ in the outflow region of the

deep convective cloud system, the ice begins to sublime (step e). After complete sublimation, the “naked”, ice-cloud-processed SOA particle is left behind (step f). This particle can have a very fluffy structure with large internal cavities or pores — open spaces that were previously occupied by ice, as revealed by the exemplary ESEM image of a cloud-processed α -pinene-derived SOA particle subjected to the atmospheric freeze-drying cycle in an earlier AIDA expansion experiment (Wagner et al., 2024).

When the freeze-dried SOA particle is then again subjected to an updraft and enters an ice-supersaturated environment (stage g), its heterogeneous ice nucleation ability may be enhanced compared to the compact, unprocessed particle. On the one hand, this could be due to the much larger surface area of the fluffy, cloud-processed particle, or it could be that the open network structure contains pores suited to triggering ice formation by the pore condensation and freezing (PCF) mechanism. On the other hand, an improved ice nucleation ability could be explained by a “traditional” pre-activation mechanism, whereby some small ice residues could survive in the fluffy structure of the cloud-processed particle, even under ice-subaturated conditions, acting as ice growth sites in the following updraft. This has been demonstrated in repeated ice nucleation experiments with mineral dust particles (Knopf et al., 2006). Also, the freeze-drying cycle may leave an “imprint” of the ice lattice on the organic material, lowering the nucleation barrier for ice formation in a subsequent updraft. However, experimental evidence on this suggested enhancement of the ice nucleation ability of fluffy, porous SOA particles after the deep convective cloud-processing is still lacking. The study by Adler et al. (2013) focused on the modified optical properties of the cloud-processed SOA particles, but did not include any measurements of their ice nucleation ability. The first experimental study in this regard was the recent AIDA experiments with α -pinene-derived SOA particles, whose results will be summarized in the next section.

Before addressing these results, the second cloud-processing type, i.e., repetitive updrafts under cirrus conditions (cirrus processing), will briefly be discussed. Fig. 5.3 illustrates the degree of morphological change that can be expected by such a cloud-processing cycle, which does not include the temporary formation of cloud droplets. It largely depends on the degree of liquefaction the initially glassy particle experiences before the onset of ice nucleation. Scenario I would correspond to an initial updraft at low temperature, where the glassy SOA particle (step a) does not, even partially, liquefy before the onset of ice nucleation on the still solid particle surface by deposition nucleation (step b). The ice phase, therefore, does not penetrate the organic matrix, and the SOA particle remains more or less unaltered when the ice crystal has sublimated (step c), suggesting that its ice nucleation ability will not change substantially when again exposed to an updraft (step d). In scenario II, representing a higher temperature, the increase in temperature with associated decrease in viscosity leads to the possibility that the SOA particle will at least partially deliquesce (step b) before reaching

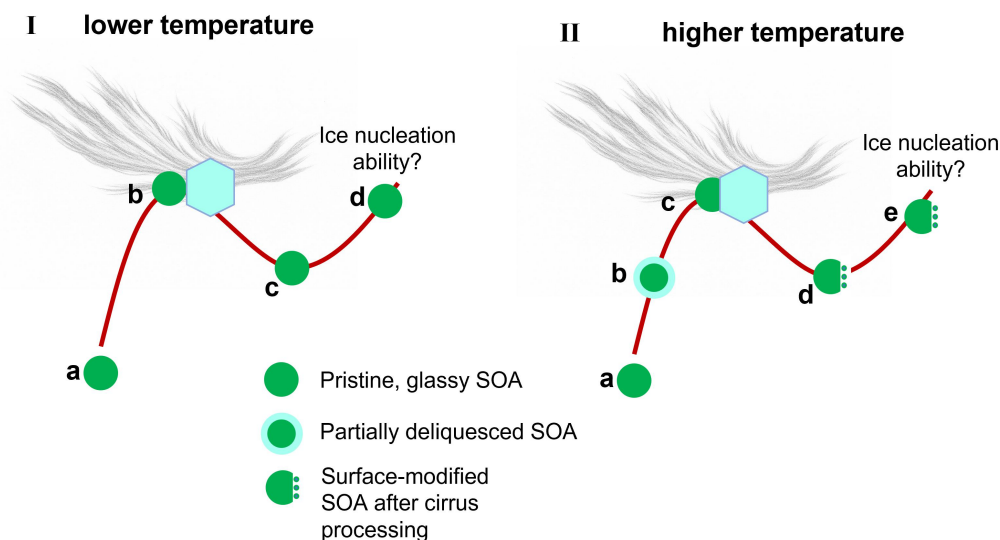


Figure 5.3: Scheme to illustrate potential morphological changes of initially compact, glassy SOA particles in repeated updrafts under cirrus conditions (cirrus cloud processing, atmospheric trajectory shown in red). Scenario I represents low-temperature cirrus conditions, where the SOA particle does not, even partially, liquefy before the ice nucleation onset. In scenario II, symbolizing high-temperature cirrus conditions, partial deliquescence takes place before ice formation. The letters, which annotate key steps in the processes, are described in detail in the text.

the ice nucleation threshold (step c). The mode of ice nucleation can then be ascribed to homogeneous or immersion freezing of the liquefied aqueous layer. Upon ice formation, the aqueous layer will freeze-concentrate, leading to reduced viscosity and re-vitrification. Thereby, the ice crystal has the chance to penetrate deeper into the organic matrix and does not just touch its surface as in scenario I. After the sublimation of ice (step d), the surface morphology might be altered and lead to a change in the particle's ice nucleation ability in a subsequent updraft (step e).

5.1.3 Earlier AIDA chamber studies on the ice-cloud processing of α -pinene-derived SOA particles

Two earlier AIDA studies have investigated the deep convective cloud and cirrus cloud processing of SOA particles, both using α -pinene as the precursor molecule (Wagner et al., 2017; Wagner et al., 2024). The results of the Wagner et al. (2024) study, focusing on the atmospheric freeze-drying process, are shown in Fig. 5.4. The black squares denote the ice nucleation onsets of the pristine, compact SOA particles before cloud-processing, as measured with the INKA and mINKA CFDC instruments sampling from the AIDA chamber at two different temperatures (217 K and 221 K). These nucleation onsets fall into the range between the homogeneous freezing and the water saturation line, and are in agreement with

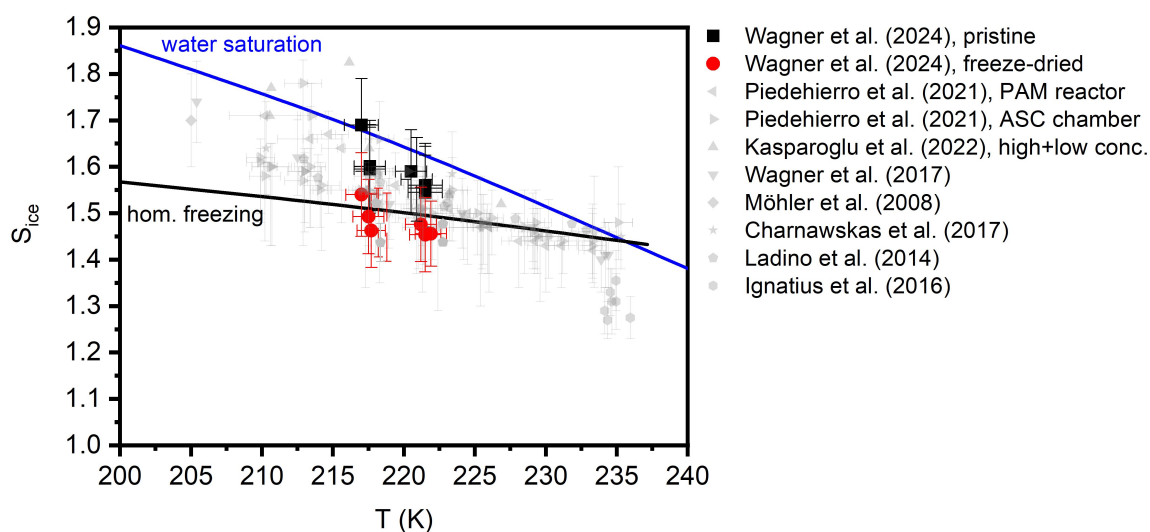


Figure 5.4: Temperature dependent onset conditions for ice formation by α -pinene-derived SOA particles, with a focus on the atmospheric freeze-drying experiments performed in the AIDA chamber by Wagner et al. (2024). The black squares are the S_{ice} thresholds for the activation of 0.1 % of the aerosol population from the Wagner et al. (2024) experiments with pristine SOA particles that have not yet been cloud processed. These data can be compared to the smaller gray symbols, which refer to ice nucleation onsets from other measurements with pristine, unprocessed SOA particles formed from α -pinene and correspond to activated fractions ranging from 0.1 to 1 %. The red circles represent the ice nucleation onsets of the porous SOA particles after simulating the freeze-drying process in the AIDA chamber. The black line denotes the threshold for the homogeneous freezing of aqueous solution droplets (Koop et al., 2000), and the blue line represents water-saturated conditions (Murphy et al., 2005).

most other literature studies that have measured the ice nucleation ability of unprocessed α -pinene-derived SOA particles (shown as gray symbols in Fig. 5.4).

After simulating the atmospheric freeze-drying cycle in the AIDA chamber, the ice nucleation onsets of the generated fluffy, porous SOA particles (see the exemplary ESEM image in Fig. 5.2) showed a small decrease by about 0.1 in the ice nucleation onsets (red circles). This points to a small improvement in the ice nucleation ability, but the nucleation onsets of the “activated”, porous SOA particles are still very close to the homogeneous freezing conditions for aqueous solution droplets. Similar observations were made in the Wagner et al. (2017) study, where α -pinene-derived SOA particles were subjected to subsequent AIDA expansion cooling runs under cirrus conditions at temperatures between 235 K and 205 K (cirrus cloud processing). These results are summarized in Fig. 5.5.

The ice nucleation onsets observed in the first simulated updraft (black squares, also included as the downward-pointing gray triangles in Fig. 5.4) show the previously discussed

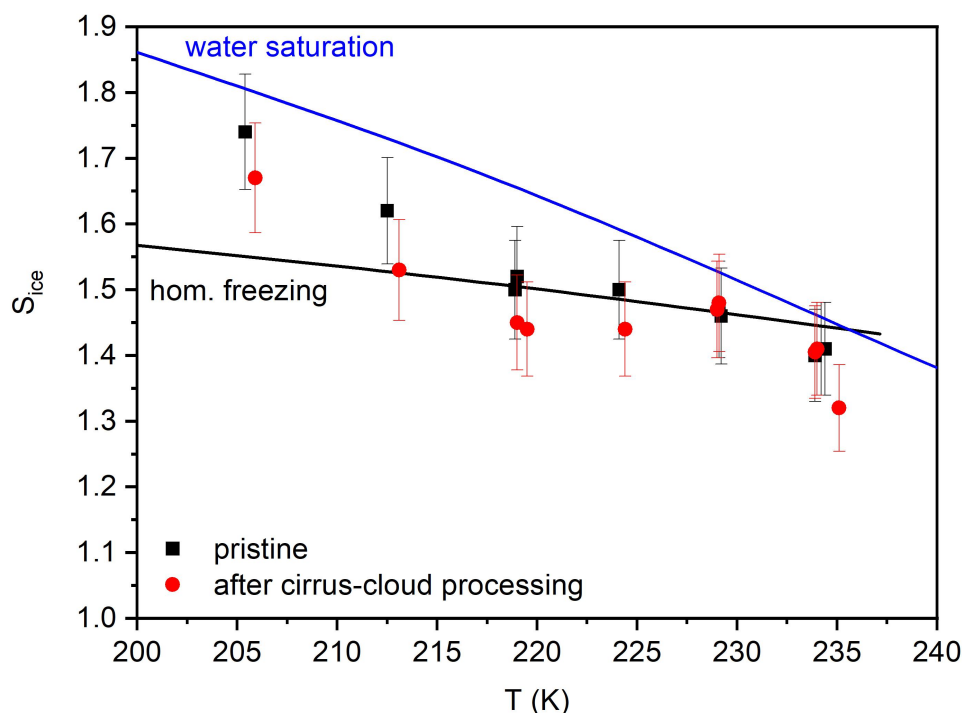


Figure 5.5: Ice nucleation onsets of α -pinene-derived SOA particles observed in repetitive AIDA expansion cooling runs conducted under cirrus conditions (Wagner et al., 2017). Black squares represent the ice nucleation behavior observed in the first simulated updraft with pristine SOA particles, while the red circles correspond to the subsequent updraft conducted after the sublimation of the ice crystals formed in the first run. The black line denotes the threshold for the homogeneous freezing of aqueous solution droplets (Koop et al., 2000), and the blue line represents water-saturated conditions (Murphy et al., 2005).

poor heterogeneous ice nucleation ability of the pristine, unprocessed SOA particles. The red circles indicate how the ice nucleation behavior has changed upon the first nucleation event, i.e., cirrus cloud processing, and correspond to the nucleation onsets in subsequent AIDA expansion cooling experiments conducted after the ice crystals from the first run had sublimated. Over the whole temperature range, only a very small change in the ice nucleation behavior can be observed. In several cases, the S_{ice} onset is reduced by a small amount of about 0.05 – 0.10 in the second run, but still lies, as discussed above, close to the homogeneous freezing line. There is also no pronounced difference in the results for “warmer” cirrus temperatures (235 K to 220 K) compared to the low-temperature end of the measurement range (220 K to 205 K), as might be conceivable based on the considerations regarding the sketch shown in Fig. 5.3. A closer discussion of these earlier AIDA results will be given later, after presenting the results of the new experiments conducted in this thesis.

5.1.4 Motivation for a new set of ice-cloud-processing experiments

At first glance, the results presented above with α -pinene as the SOA precursor show no reason to change Kasparoglu et al. (2022)'s recommendation to treat pure SOA particles as ice-inactive, since the enhancement observed after ice-cloud processing was small. However, results for a single SOA precursor type cannot be generalized. A key factor in the ice-cloud processing cycles is the temperature- and humidity-dependent viscosity of the SOM. This controls whether and to what degree a porous structure can form and be maintained, and whether cavities will partially or fully collapse during the particles' atmospheric trajectory. The viscosity depends on the molar mass, type, and number of functional groups of the many semi and low-volatile compounds that can condense to form an intricate organic mixture (Berkemeier et al., 2014; Galeazzo et al., 2021; Grayson et al., 2016; Koop et al., 2011; Petters et al., 2019). As one would expect, viscosity varies considerably depending on the type of SOA precursor. Even for a given precursor type, however, viscosity also depends on SOA formation conditions, such as RH, SOA mass concentration, and the type of oxidant (e.g., O_3 , OH or NO_3 radicals) (Grayson et al., 2016; Kiland et al., 2023; Petters et al., 2019).

Of the many possible ways to build on the previous AIDA ice-cloud processing experiments, the decision was made here to use a different SOA precursor, namely isoprene. The atmospheric significance of isoprene has already been highlighted in Chapter 4, where it was used as a relevant precursor type to study the deactivation of the intrinsic ice nucleation ability of dust particles by a coating with SOM. Given the high levels of isoprene emissions in regions with intense convective activity, such as the Amazon and the Asian monsoon area, it is crucial to understand how isoprene-derived SOA particles form and are processed in deep convective clouds. This is important not only from the perspective of new particle formation and growth (Bardakov et al., 2021; Curtius et al., 2024; Shen et al., 2024b), but also with regard to changes in their ice nucleation potential. Therefore, there is a realistic chance that the cloud cycling simulations carried out in the AIDA chamber have a real counterpart in the atmosphere.

The use of isoprene as the SOA precursor provides the opportunity to investigate how a modified particle viscosity affects the results of the cloud-cycling simulations in the AIDA chamber in comparison to those conducted earlier with α -pinene. It is generally found that isoprene-derived SOA particles have a lower viscosity than α -pinene particles (Galeazzo et al., 2021), and will therefore already liquefy at lower RHs (Bateman et al., 2015; Berkemeier et al., 2014; Pajunoja et al., 2015). These aspects will be discussed in more detail when the AIDA results are described.

5.2 Aerosol particle generation

Isoprene-derived SOA particles were generated at room temperature and in dry synthetic air, under well-controlled and repeatable reaction conditions in the Aerosol Preparation and Characterization (APC) chamber (see Fig. 3.1). For each experiment, the process was started by adding about 30 ppmv of ozone to the aerosol vessel, which was produced using the silent discharge generator (Semozon 030.2, Sorbios) in pure oxygen. Subsequently, 48 ppmv of isoprene were added by evaporating the necessary amount of the substance into a 1 L glass bulb, which was then flushed with dry synthetic air and transferred to the APC chamber. After 1 hour reaction time in the APC chamber, the nucleated SOA particles had grown to a mobility diameter of approximately 300 nm, accompanied by number concentrations $> 10^5 \text{ cm}^{-3}$.

Thereafter, the SOA particles were transferred from the APC to the AIDA chamber, which was appropriately conditioned for the type of cloud-processing cycle to be performed. These conditions will be specified and discussed in more detail below. The particle transfer was achieved by enabling a $30 \text{ std L min}^{-1}$ sample flow from the initially particle-free AIDA chamber, opening the 25 mm diameter stainless steel connection tube between the two chambers (see Fig. 3.1, transfer line labeled T1) and adding a corresponding $30 \text{ std L min}^{-1}$ flow of synthetic air to the APC chamber to balance the pressure. After a flushing period of 15 minutes, particle transfer was stopped once the number concentration of SOA particles in the AIDA chamber had reached a value of approximately 1200 cm^{-3} . Representative number size distributions from different experiments, as measured by the Scanning Mobility Particle Sizer (SMPS) sampling from the AIDA chamber after particle transfer, are shown in Fig. 5.6. They underline the high repeatability of the particle generation and transfer conditions, yielding consistent median electrical mobility diameters, D_{me} , in the narrow range between $0.28 \mu\text{m}$ and $0.33 \mu\text{m}$. The composition of the SOA particles in AIDA was characterized with a high-resolution time-of-flight Aerosol Mass Spectrometer (HR-ToF-AMS). The mean oxygen-to-carbon (O:C) ratio of the SOA particles inferred from the HR-ToF-AMS measurements was 0.69, compared to a value of 0.35 reported by Wagner et al. (2017) for α -pinene-derived SOA particles.

5.3 AIDA simulation of deep-convective cloud cycling

5.3.1 Experimental protocol and observed morphological changes

The “real” atmospheric deep-convective cloud processing of the SOA particles sketched in Fig. 5.2 involves a large dynamic temperature and humidity range, from warm and humid conditions at the initial CCN activation of the SOA particles to dry and cold air in the outflow of deep convection. The classic AIDA chamber has the limitation that its dynamic temperature

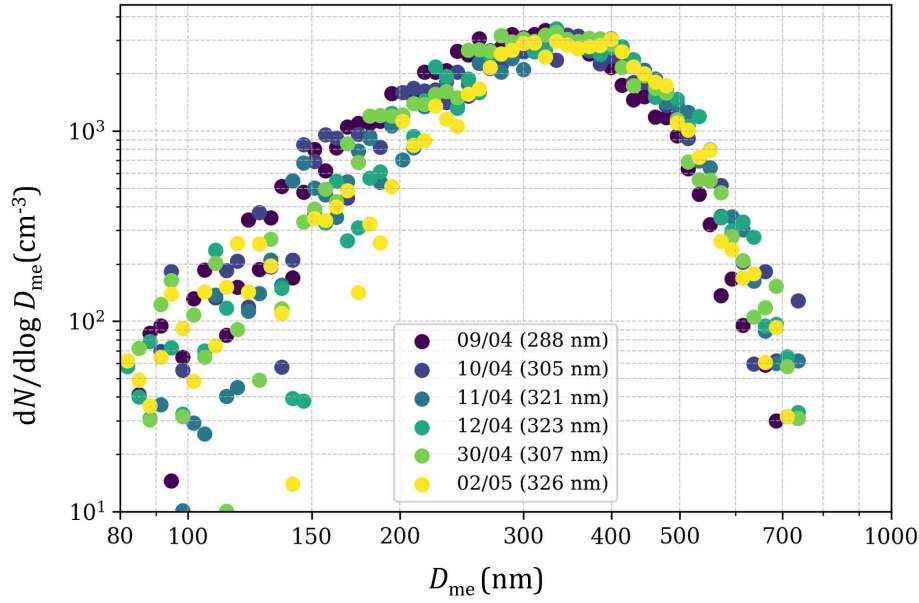


Figure 5.6: Aerosol particle number size distributions measured by the SMPS connected to the AIDA chamber for all experiment days. Median particle diameters for each day are indicated in parentheses.

range, or, more precisely, the decrease in the gas temperature that can be achieved in a standard expansion cooling cycle (see Fig. 3.6), is at most about 10 K. This is because the temperature of the walls of the cloud chamber cannot be actively controlled. While the gas temperature decreases during a simulated updraft in the well-mixed part of the vessel, the temperature of the walls remains nearly constant. This, in turn, leads to an increased heat flux from the walls into the volume. Initially, this reduces the cooling rate compared to adiabatic conditions, and ultimately, it completely stops the cooling, even though pumping continues. In an AIDA simulation of the deep-convective cloud processing, the initial CCN activation of the SOA particles, therefore, cannot be conducted at high temperatures. Instead, it must be performed at sufficiently low sub-zero temperatures, so that the homogeneous freezing temperature of approximately 235 K can still be reached during continued pumping. As outlined by Wagner et al. (2024), an initial temperature of 243 K fulfills these requirements.

Another factor to be considered is the appropriate initial RH. When starting at 243 K, a high initial RH is required so that $RH > 100\%$ conditions during updraft are already reached a few degrees above the homogeneous freezing threshold, i.e., that CCN activation occurs before ice nucleation. Therefore, the AIDA chamber was humidified to almost ice-saturated conditions with $S_{ice} \approx 0.96$ and $S_{liq} \approx 0.72$. During the simulated updraft started at 243 K, CCN activation at $S_{liq} > 1$ is then typically observed at 239 K, still 4 K above the homogeneous freezing conditions. With these pre-remarks on the appropriate conditioning of the AIDA chamber, it is now time to focus on the measurement data during the deep-convective cloud processing, which are compiled in Fig. 5.7.

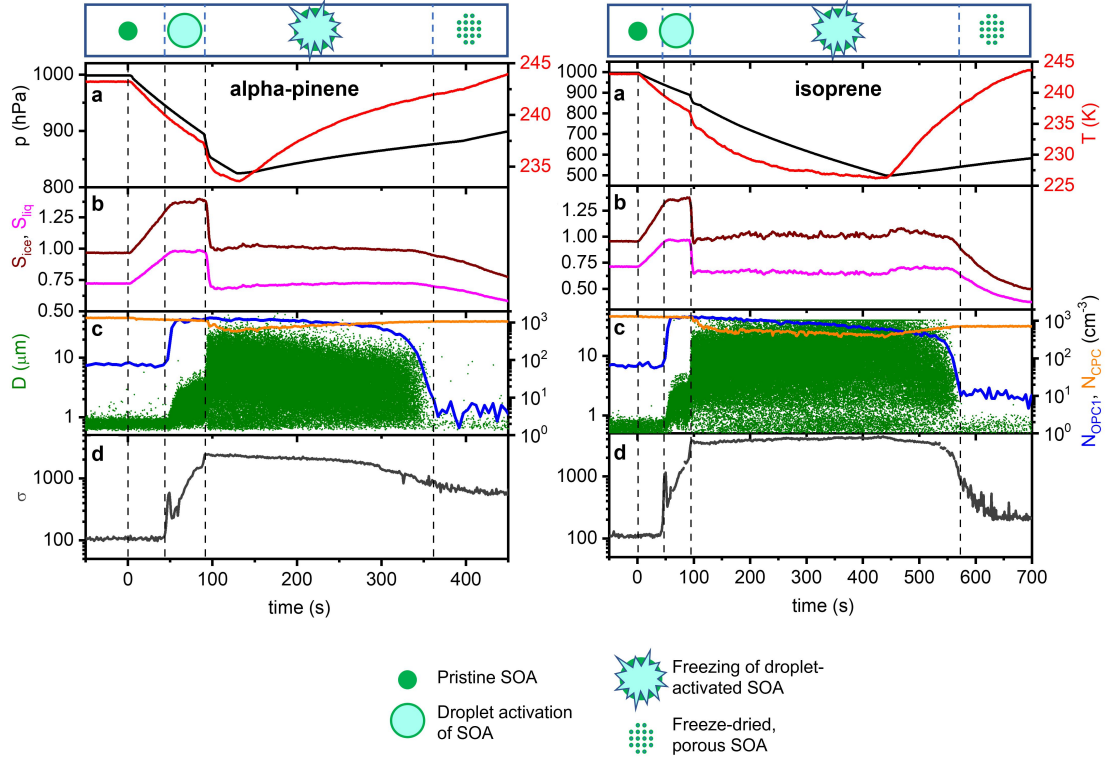


Figure 5.7: AIDA measurement data during deep-convective cloud processing experiments with SOA particles generated from α -pinene (left part, data from Fig. 4 in Wagner et al. (2024)) and isoprene (right, this thesis). The pictograms on top symbolize the various processing steps (see Fig. 5.2). The experimental time is given in seconds with respect to the start of pumping at time zero. In each part, the four panels a – d show the following data. a: AIDA pressure (black line) and mean gas temperature (red line); b: saturation ratios with respect to ice (S_{ice} , brown line) and supercooled liquid water (S_{liq} , magenta line); c: single particle scattering data of the OPC1 (green dots), total number concentration of aerosol particles from the CPC measurements (N_{CPC} , orange line), and number concentration of particles $> 0.5 \mu\text{m}$ measured by the OPC1 (N_{OPC1} , blue line); d: forward-to-backward (2° - 178°) scattering ratio measured by SIMONE (gray line).

Fig. 5.7 directly compares the AIDA data of the experiments with α -pinene as SOA precursor from Wagner et al. (2024) (left part) with the new isoprene-derived SOA experiments from this thesis (right part), where the experimental procedure has been slightly modified as discussed in the following. In both parts, panel a shows the basic chamber parameters, like the pressure and the gas temperature during the expansion experiment. Panel b displays the saturation ratios with respect to water (S_{liq}) and ice (S_{ice}) derived from the water vapor measurements using the Tunable Diode Laser (TDL). The single particle scattering data from the welas OPC1 are represented by the green dots in panel c, corresponding to a calibrated particle diameter on the left axis. Panel c additionally shows the total aerosol particle number concentration measured by the Condensation Particle Counter (CPC) (N_{CPC} , orange line), and the number

concentration of particles with optical diameters above 0.5 μm detected by the OPC1 during the cloud processing experiments (N_{OPC1} , blue line) to detect the progress of droplet activation or ice nucleation. Panel d shows the forward-to-backward (2° - 178°) scattering ratio measured by the SIMONE instrument (σ , gray line, calibrated according to Mie calculations during the periods of supercooled liquid cloud droplets (Schnaiter et al., 2012)). σ was found to be a sensitive parameter to reveal the morphological change of the SOA particles during cloud-processing. The time on the x -axis represents the time in seconds, after the start of the AIDA expansion experiment at $t = 0$. The pictograms on top illustrate the various stages of the deep-convective cloud cycling in analogy to the sketch in Fig. 5.2.

As motivated above, the static conditions before the expansion cooling was started at $t = 0$ (first vertical dashed line in both parts of Fig. 5.7) correspond to $T = 243 \text{ K}$ and $S_{\text{ice}} = 0.96$ ($S_{\text{liq}} = 0.72$). Only a small fraction of the sub-micron-sized SOA particles extend into the measurement range of the OPC1, meaning that the ratio $N_{\text{OPC1}}/N_{\text{CPC}}$ is only 6 % for α -pinene and 5 % for isoprene. The increase in RH with the start of expansion cooling leads to CCN activation of the SOA particles at $S_{\text{liq}} > 1$ (second vertical line), approximately, as noted above, at a gas temperature of about 239 K. The presence of super-micron-sized cloud droplets can be clearly seen in the single particle data of the OPC1. Furthermore, after droplet activation, N_{OPC1} and N_{CPC} closely agree, indicating that almost all seed aerosol particles had been activated.

To detect a clear change in the SOA particle measurement data due to a change in morphology, it is essential to ensure that all seed particles undergo the cloud processing steps simulated in the AIDA chamber. The agreement between N_{OPC1} and N_{CPC} shows that this was indeed successful for the first step, i.e., the CCN activation of the aerosol particles, but it must also be assured for the second step, i.e., the freeze-drying step involving the nucleation of ice. In practice, this means that all of the supercooled cloud droplets would ideally freeze homogeneously. This requires a particular experimental “trick”. If one would continue with a moderate pumping speed or cooling rate, the AIDA gas temperature would slowly fall below the homogeneous freezing threshold at about 235 K. Due to unavoidable temperature inhomogeneities in the chamber, some ice crystals would start to form in slightly colder parts of the chamber and consume the reservoir of still unfrozen cloud droplets through the Wegener–Bergeron–Findeisen process (Storelvmo et al., 2015). Consequently, only a small percentage of the cloud droplets would actually freeze, or, in other words, only a small subset of the aerosol population would undergo atmospheric freeze-drying in the simulated deep-convective cloud processing. Hence, a so-called “super-expansion” was performed just at the instance when the AIDA temperature approached the homogeneous freezing threshold (third vertical line). Here, a valve was opened to the by now evacuated APC chamber (see Fig. 3.1, T2 connection line), serving as an empty buffer volume to induce an almost instant

pressure drop in the AIDA vessel by another 30 hPa to 40 hPa, leading to an equally instant temperature drop by another 2 K to 3 K. As such, the whole chamber volume was thereby instantly exposed to homogeneous freezing conditions, assuming that this would lead to the freezing of all cloud droplets. The aspherical shape of the formed ice crystals results in a much broader distribution of particle sizes in the OPC1 records. Furthermore, upon freezing the RH drops almost instantly from water-saturated ($S_{\text{liq}} = 1$) to ice-saturated ($S_{\text{ice}} = 1$) conditions. Most importantly, during the phase change from cloud droplets to ice crystals, the number concentration N_{OPC1} of hydrometeors indeed remained unchanged (blue lines in panel c), verifying that all cloud droplets did indeed freeze.

From the “super-expansion” onwards, the experimental protocol for the α -pinene and isoprene experiments differed. In the case of α -pinene-derived SOA particles, pumping was stopped shortly after the super-expansion and the chamber was refilled to ambient pressure with dry synthetic air to sublime the ice crystals. This simulated the processes occurring in the outflow region of deep convection (see Fig. 5.2). After the completed sublimation of ice (fourth vertical line), the fluffy, porous SOA particles are left behind, as shown in the exemplary ESEM image in Fig. 5.2. Apart from the direct evidence provided by the ESEM images, two further sets of AIDA measurement data indicate a change in morphology during cloud-processing related to the particles’ modified optical properties. Firstly, after cloud processing, the fluffy SOA particles scatter much less light into the side-scattering detection angles of the OPC1. In other words, they largely “disappear” from the OPC1 records. As a result, for the α -pinene-derived SOA particles, the ratio $N_{\text{OPC1-to-}N_{\text{CPC}}}$ decreases from 6 % before cloud-processing to 0.6 % after. Secondly, the forward-to-backward scattering ratio (σ) also reacts strongly to the changes in morphology. It first strongly increases during the expansion cooling when the super-micron-sized cloud droplets and ice crystals are formed, with some Mie oscillations visible in the early stages of droplet growth. However, the value remains much higher even after sublimation of the ice. It is about five times higher for the fluffy, cloud-processed particles than for their compact, pristine counterparts.

The two pieces of measurement data, i.e., the ratio $N_{\text{OPC1-to-}N_{\text{CPC}}}$ and σ , therefore provide an immediate indication, i.e., a sort of “quality control”, of whether a freeze-drying simulation in the AIDA chamber has successfully generated porous particles, well before the results of the more time-consuming ESEM analysis can be obtained. When the first deep-convective cloud cycling experiment was performed with isoprene-derived SOA particles in exactly the same way as before with α -pinene, the values of these two quality markers changed very little before and after cloud processing (data not shown). This precursor-type-dependent change is most likely related to the different viscosity behavior of the α -pinene- and isoprene-derived SOA particles. This must be discussed alongside the fact that, unlike the conditions in the real atmosphere, certain limitations of the AIDA chamber also come into play during

the final stage of the deep-convective cloud processing simulation. While the AIDA gas temperature had temporarily dropped to about 233 K during expansion cooling in the case of α -pinene, this temperature could not be maintained while the ice crystals sublimate to release the cloud-processed SOA particles for the further, time-consuming analysis steps involving the collection of ESEM filters and probing the particles' ice nucleation ability with the CFDCs. The cloud-processed SOA particles are therefore not strictly released into a "cold" atmosphere; rather, the AIDA temperature quickly relaxes back to that of the "warm" walls, which is 243 K. After refilling and temperature equilibration, the RH is lower than before expansion cooling, because some of the humid air (with $S_{\text{liq}} = 0.72$) was pumped out and replaced with dry air during refilling. Note here that the AIDA chamber was initially carefully humidified to near ice-saturated conditions, while avoiding the formation of an ice layer on the walls, which could act as a water reservoir during refilling. For the standard procedure applied in the α -pinene cloud-processing experiments (shown in the left part of Fig. 5.7), the RH decreased from 72 % to 61 % after refilling. For the SOM formed from the ozonolysis of α -pinene, the AIDA conditions with 243 K and $S_{\text{liq}} = 0.61$ obviously fall within the highly-viscous/glassy range of the phase diagram, because the fluffy, porous particle structure formed by the atmospheric freeze-drying step could be maintained. However, in the case of isoprene, the lower viscosity of the SOM generated compared to α -pinene might have caused the porous structure to collapse again under these conditions, resulting in nearly identical values for the $N_{\text{OPC1-to-NCPC}}$ ratio and σ to those before cloud-processing.

To help stabilize the fluffy, porous particle morphology also in the case of isoprene, the experimental protocol was changed as shown in the right part of Fig. 5.7. While there is no fast and practicable way to lower the temperature to which the cloud-processed SOA particles equilibrate, it is possible to expose them to drier air, and thereby reduce their viscosity. Therefore, unlike with α -pinene, the AIDA chamber was not immediately refilled with dry air after the "super-expansion". Instead, pumping continued for an extended period of time until the chamber pressure had decreased to about 500 hPa. Only then were the ice crystals sublimated by refilling the chamber to ambient pressure. By pumping out a larger amount of humid air and replacing it with dry air, the RH after refilling and temperature equilibration to 243 K was only 41 % compared to 61 % in the original procedure. With that modified procedure in the final cloud-processing step, significant changes in the $N_{\text{OPC1-to-NCPC}}$ ratio and σ were also observed in the isoprene cloud-processing experiment, although the magnitude of the changes was smaller compared to α -pinene. For isoprene, the $N_{\text{OPC1-to-NCPC}}$ ratio decreased from 5 to 1.5 % after cloud-processing (6 to 0.6 % in the case of α -pinene), and σ increased by a factor of 2 (factor 5 in the case of α -pinene). Fig. 5.8 shows that the modified AIDA measurement data, i.e., the lower value for N_{OPC1} and the higher value for σ , remained near constant for long time periods after cloud-processing, both for α -pinene and

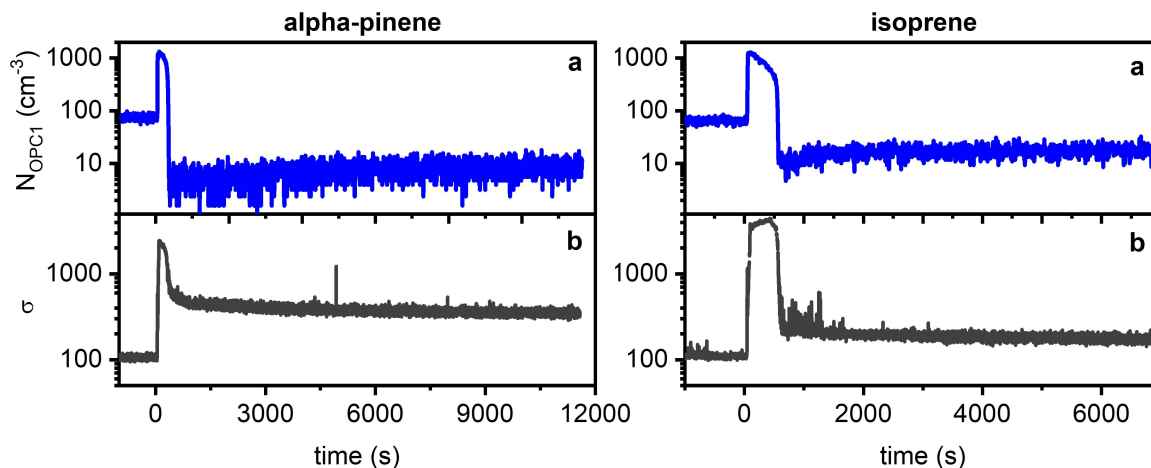


Figure 5.8: Long-term trend in the number concentration of $> 0.5 \mu\text{m}$ -sized particles measured by the OPC1 (panels a) and the forward-to-backward scattering ratio σ (panels b) for the α -pinene (left part) and isoprene (right part) cloud-processing experiments.

isoprene. During this time, the filter sampling for the ESEM analysis and the ice nucleation measurements with CFDCs were performed.

The reduced magnitude in the change of the $N_{\text{OPC1-to-}N_{\text{CPC}}}$ ratio and σ between the α -pinene and isoprene experiments also manifests itself in the degree of “fluffiness” or porosity seen in the ESEM images of the filter-collected SOA particles. The top part of Fig. 5.9 shows the ESEM images from the α -pinene experiments already published in Wagner et al. (2024). The lower part shows representative ESEM images of isoprene-derived SOA particles from this work, with filter-sampling periods before cloud-processing (“pristine” SOA) and after cloud-processing (“freeze-dried” SOA). The pristine particles in both the α -pinene and isoprene experiments are nearly spherical. Atmospheric freeze-drying leads to a very pronounced change in particle morphology for α -pinene, yielding highly fluffy particles with a network of large cavities and an overall highly disrupted structure. The structure reflects that the organic material, initially dissolved in the cloud droplets after CCN activation, was rejected and redistributed over the irregular structure of the ice crystal after freezing, and became vitrified. The sublimation of ice and the re-equilibration of the particles at 243 K and $S_{\text{liq}} = 0.61$ obviously did not alter the open network structure, i.e., the high viscosity of the freeze-concentrated SOM prevented its collapse. In the case of isoprene with a lower viscosity of the generated SOM, the ESEM images of the freeze-dried particles also show a clearly irregular morphology, but the highly open network structure from α -pinene is missing. As outlined above, the experimental protocol was altered to help stabilize the porous structure in the isoprene experiments. However, it seems obvious that some re-compaction or re-collapse still occurred during freeze-drying, where the particles were exposed to varying

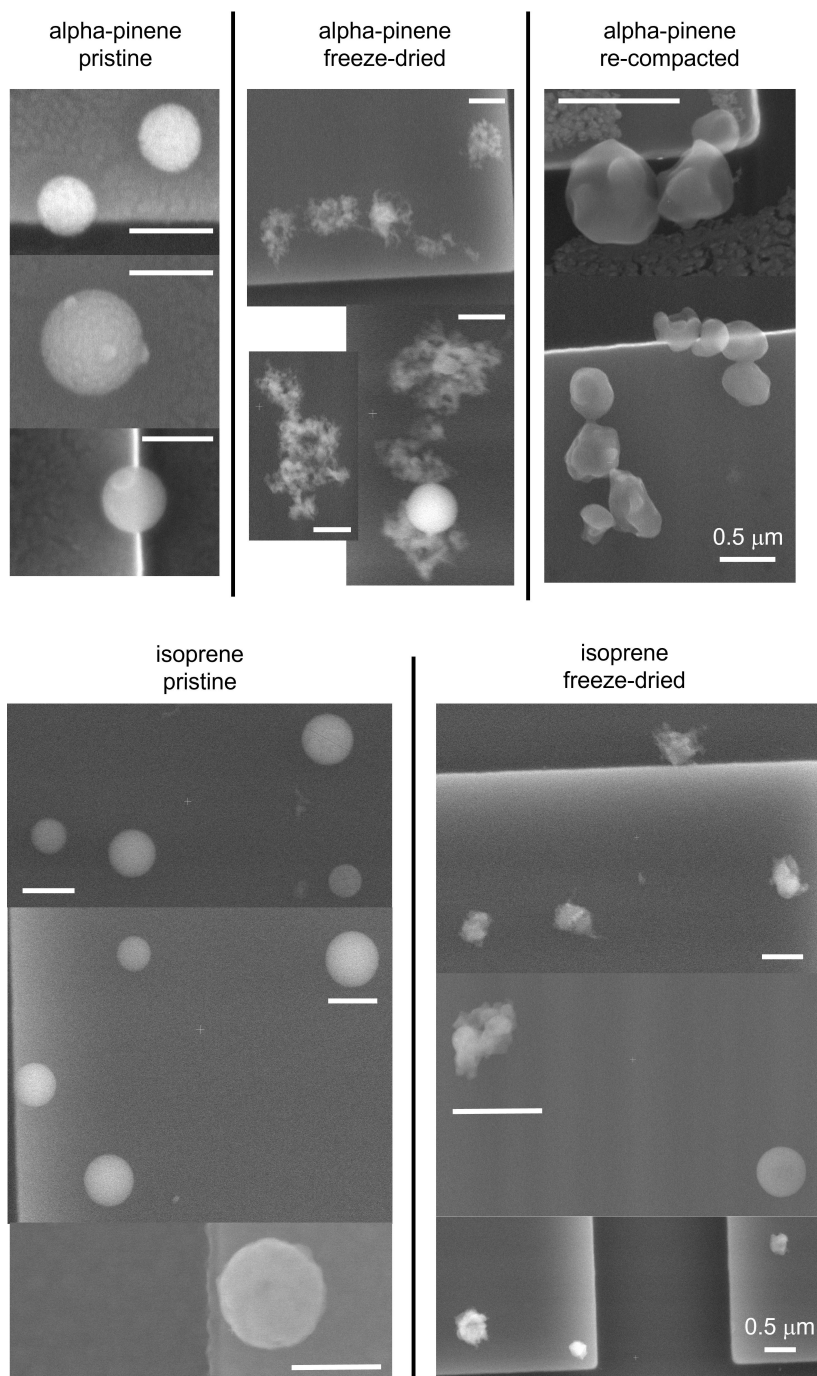


Figure 5.9: ESEM images of filter-collected SOA particles. Top part: Results from Wagner et al. (2024) for pristine, freeze-dried, and re-compacted SOA particles from the ozonolysis of α -pinene. Bottom part: Images from this thesis for pristine and freeze-dried isoprene-derived SOA particles. Images are shown in different magnification with the white bar showing a length scale of 0.5 μm . See text for details.

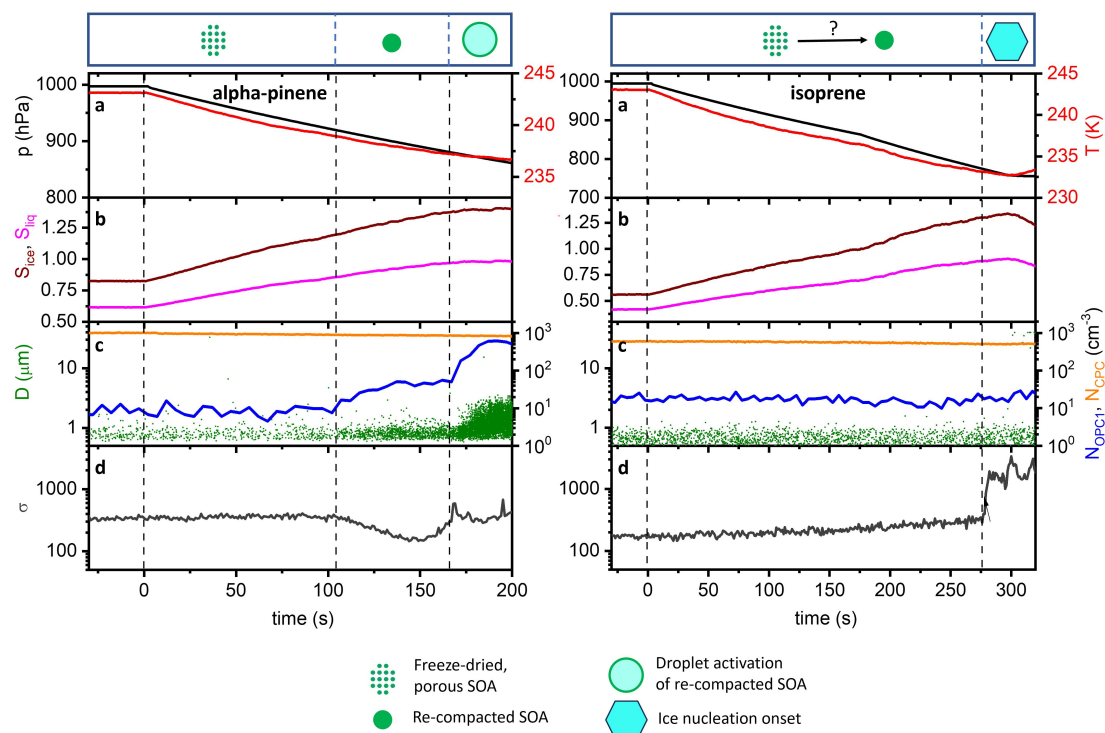


Figure 5.10: AIDA measurement data during the so-called “re-compaction” step that was carried out after the characterization of the porous, freeze-dried particles. The individual panels show the same types of measurement data as in Fig. 5.7. The re-compaction step in the case of α -pinene (left part, data from Fig. 6 in Wagner et al. (2024)) was stopped at the CCN activation of the seed aerosol particles (third vertical line). In the case of isoprene (right part, data from this thesis), the starting RH was lower so that CCN activation was not observed. Expansion cooling was stopped here at onset of ice nucleation on the seed aerosol particles (second vertical line).

temperature and humidity conditions before being ultimately stabilized at 243 K and $S_{\text{liq}} = 0.41$ (Fig. 5.7). As already indicated above, the more compact morphology of the freeze-dried isoprene-derived SOA particles might explain the smaller changes in the $N_{\text{OPC1-to-NCPC}}$ ratio and σ . Nonetheless, a clear change in particle morphology was also successfully induced for isoprene-derived SOA particles, providing an opportunity to explore the associated effect on the particles’ ice nucleation ability.

Before moving on to the ice nucleation measurements in the next section, a further processing step of the SOA particles will briefly be described, which was already performed by Wagner et al. (2024). The left part of Fig. 5.10 shows the AIDA measurement data from Wagner et al. (2024) for a so-called “re-compaction” step, which was conducted after characterizing the fluffy, porous α -pinene-derived SOA particles formed in the freeze-drying step. “Re-compaction” involved a gentle AIDA expansion where the RH was slowly increased. At a certain threshold (second vertical line), the increase in RH, with the associated decrease

in particle viscosity, led to a collapse or compaction of the porous network structure. This resulted in a reverse trend in the AIDA measurement data compared to the freeze-drying step: the re-compacted SOA particles started to “re-appear” in the OPC1 records, leading to an increase in N_{OPC1} , and the forward-to-backward scattering ratio σ decreased to a value representative of compact particles. The re-compaction expansion was stopped with the onset of the CCN activation (third vertical line), and the AIDA chamber was refilled for another characterization period. ESEM images of the particles collected after the re-compaction step (top part of Fig. 5.9) indeed showed that the open network structure had disappeared completely, and that the particles were again compactly shaped but not completely spherical, appearing slightly bulbous.

The AIDA measurement data from a similar re-compaction expansion carried out with the freeze-dried isoprene-derived SOA particles are shown in the right part of Fig. 5.10. During the moderate expansion, there are no abrupt changes in N_{OPC1} and σ that point to a clear re-compaction step. However, it should be noted that the particle morphology of the freeze-dried isoprene-derived SOA particles was already clearly more compact compared to α -pinene, meaning that the expected changes in N_{OPC1} and σ would also be much smaller. Due to time constraints, it was not possible to perform filter sampling for ESEM analysis in the case of isoprene after re-compaction, so that it remains speculative how much structural change the particles have experienced. However, ice nucleation measurements using the CFDCs were also conducted after the re-compaction step.

5.3.2 Change of the ice nucleation ability of the deep-convective cloud processed SOA particles

Fig. 5.11 shows the ice nucleation measurements for the isoprene-derived SOA particles with mINKA (part a, left) and INKA (part b, right). In order to conserve the structural change of the particles induced by cloud processing, the particles were sampled from the 243 K-cold AIDA chamber through an equally cold, actively cooled sampling line before entering the CFDCs. The actual humidity ramps were conducted under cirrus conditions at temperatures of around 220 K. The measurement data reflect the spectrum of the ice-active fraction of the aerosol population (AF) as a function of the ice saturation ratio (S_{ice}). The color-coding of the spectra refers to the sampling periods or characterization stages: black lines correspond to the pristine SOA particles, red lines to the freeze-dried particles after the simulated deep-convective cloud processing, and blue lines to the re-compacted particles. mINKA scans were conducted at two slightly different temperatures (solid and dashed lines, no measurement could be conducted after re-compaction at 222 K), while INKA scans were only performed at a single temperature.

The CFDC data reveal only subtle changes in the ice nucleation ability during cloud-processing. In accordance with previous literature (see Section 5.1.1), the pristine, compactly

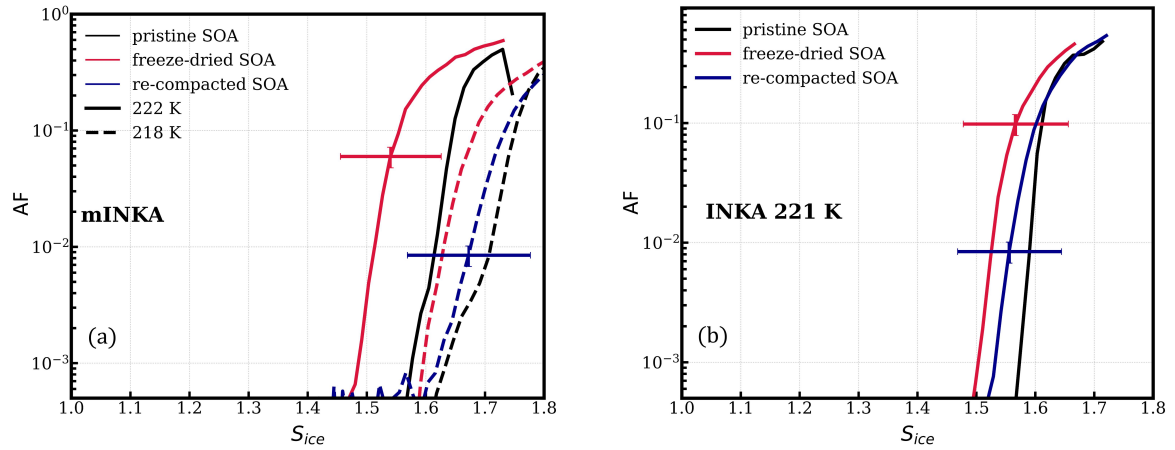


Figure 5.11: Ice nucleation measurements with mINKA (panel (a)) and INKA (panel (b)) during the atmospheric freeze-drying experiment with isoprene-derived SOA particles. The color coding refers to the different stages of the experiment (black: pristine particles, red: freeze-dried particles, blue: re-compacted particles). mINKA scans were conducted at two slightly different temperatures (solid and dashed lines), whereas INKA scans were only conducted at a single temperature. Horizontal and vertical error bars correspond to the uncertainties in the ice saturation ratio and the activated fraction (AF), respectively.

shaped isoprene-derived SOA particles are rather ice-inactive, only showing a marked increase in the ice-active fractions above ice saturation ratios of about 1.55. After deep-convective cloud processing, the activated fraction (AF) vs. S_{ice} spectra of the freeze-dried, moderately porous SOA particles are slightly shifted to lower ice saturation ratios by an absolute amount of about 0.05 – 0.10. This subtle improvement in the particles' ice nucleation ability is partially reversed by the re-compaction step, resulting in a very slight shift in the AF vs. S_{ice} spectra again towards higher S_{ice} values. As can be seen from the uncertainty estimates in Fig. 5.11, these small shifts on the S_{ice} - scale are of the same order of magnitude as the absolute uncertainty in S_{ice} itself in the CFDC measurements. The latter, as discussed in Section 3.3, is mainly governed by the uncertainty of the temperature at the aerosol lamina and the uncertainty of the thickness of the coating layer of ice on the walls of the CFDCs. However, the CFDC measurements shown in Fig. 5.11 were performed consecutively, with no re-icing of the instruments between stages. Therefore, the small relative changes observed in the different characterization stages are expected to be robust.

These new ice nucleation measurements for isoprene-derived SOA particles can now be compared with those from the Wagner et al. (2024) study involving α -pinene in the S_{ice} vs. T diagram (Fig. 5.12). As in Fig. 5.4, the solid black squares represent the ice nucleation onsets of compactly shaped α -pinene-derived SOA particles (pristine or re-compacted), while the solid red circles represent the onsets of the highly fluffy freeze-dried particles after

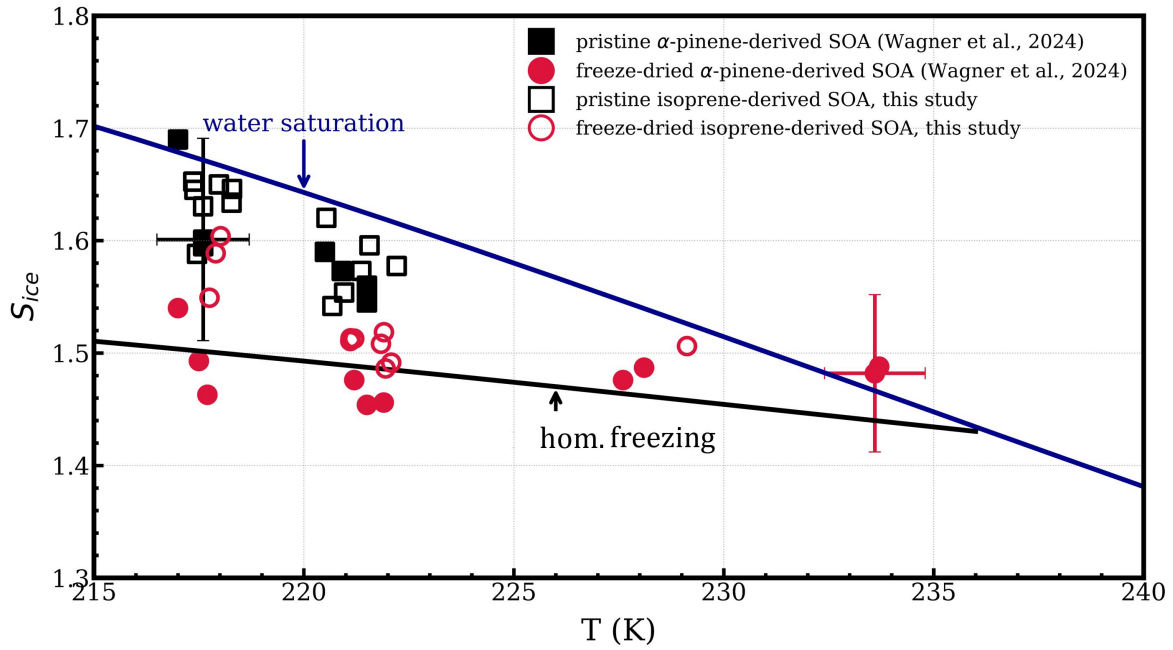


Figure 5.12: Temperature dependent onset conditions for ice formation by isoprene- (this thesis, open symbols) and α -pinene (Wagner et al., 2024, solid symbols) derived SOA particles. The black squares are the S_{ice} thresholds for the activation of 0.1 % of the pristine, unprocessed SOA particles. The red circles represent the ice nucleation onsets of the porous SOA particles after simulating the freeze-drying process in the AIDA chamber. The blue line represents water-saturated conditions (Murphy et al., 2005) and the black line denotes the threshold for the homogeneous freezing of aqueous solution droplets (Koop et al., 2000).

deep-convective cloud processing. Open black squares and open red circles show the same data obtained in this thesis for isoprene-derived SOA particles.

The measurement data for both types of SOA precursors are highly consistent. The new experiments in this thesis therefore confirm that freeze-drying, i.e., deep-convective cloud processing, slightly improves the ice nucleation ability of SOA particles, without, however, pushing the ice nucleation onsets significantly below homogeneous freezing conditions. As already discussed above, the reason behind this small improvement remains a matter of speculation. Although the increase in particle surface area after freeze-drying was much higher for α -pinene than for isoprene, the improvement in ice nucleation ability was similar. Also, when considering the PCF mechanism, the size, shape, and quantity of the pores formed in the experiments with the two SOA precursors, as seen in the ESEM images in Fig. 5.9, are likely to differ significantly without affecting the ice nucleation ability to a similar degree. One possible interpretation is that the enhancement of the ice nucleation ability after cloud-processing is due to a small “classic” pre-activation or memory effect, e.g., a

residual “footprint” of ice on the organic material, which acts for both types of SOA precursors independent of the morphological details of the freeze-dried particles.

5.4 Simulation of cirrus cloud processing

5.4.1 Experimental protocol and observed morphological changes

This chapter now addresses the possibility that SOA particles may experience repeated updrafts under cirrus conditions. The first ice nucleation event may alter the surface morphology, as illustrated in Fig. 5.3 (scenario II), possibly affecting the particles’ ice nucleation ability in succeeding updrafts (cirrus processing). In the previous cirrus-processing experiments with α -pinene-derived SOA particles described in Wagner et al. (2017), two repetitive AIDA expansion runs were conducted, and the ice nucleation onsets observed in the second run were compared to those of the first run with the pristine particles (see Fig. 5.5). A different approach is employed here for the new experiments with isoprene as the SOA precursor: a combination of AIDA and the CFDCs. AIDA is used to simulate the initial updraft through an expansion cooling experiment. It then acts solely as a reservoir tank for the cirrus-processed SOA particles while the CFDCs measure their ice nucleation ability.

The initial AIDA expansion run was conducted at two different temperatures: a “warm” cirrus temperature of 235 K, which has a higher likelihood of partial liquefaction of the SOA particles before ice nucleation begins (scenario II in Fig. 5.3); and a “colder” cirrus temperature of 227 K, where partial deliquescence may not occur. The AIDA measurement data for the “warm” cirrus experiment started at 235 K are shown in Fig. 5.13.

Also in this experiment, the AIDA chamber was carefully humidified to almost ice-saturated conditions with S_{ice} of about 0.95. The expansion was initially conducted with constant pumping power. After about 50 s, a small, gradual increase in the forward-to-backward scattering ratio σ (panel d) was observed, which could indicate particle growth through partial deliquescence of the SOA particles. However, as this experiment was conducted at cirrus temperatures, depositional ice nucleation on background impurity particles in the AIDA chamber could also be an explanation. This is because a very small number concentration of large ice crystals would also lead to an increase in σ . Just at the point when σ then started to increase more strongly, indicating that the onset conditions for ice nucleation on the SOA particles were reached (second vertical line in Fig. 5.13), a “super-expansion” with the evacuated APC chamber was conducted. The reason was the same as for the simulation of deep-convective cloud processing described in the previous section. The main objective was again to ensure that all the seed aerosol particles underwent cirrus processing, i.e., that an ice crystal formed on each SOA particle. With a continuous, moderate pumping speed, ice nucleation would have started locally in some colder segments of the cloud chamber. The nucleated ice

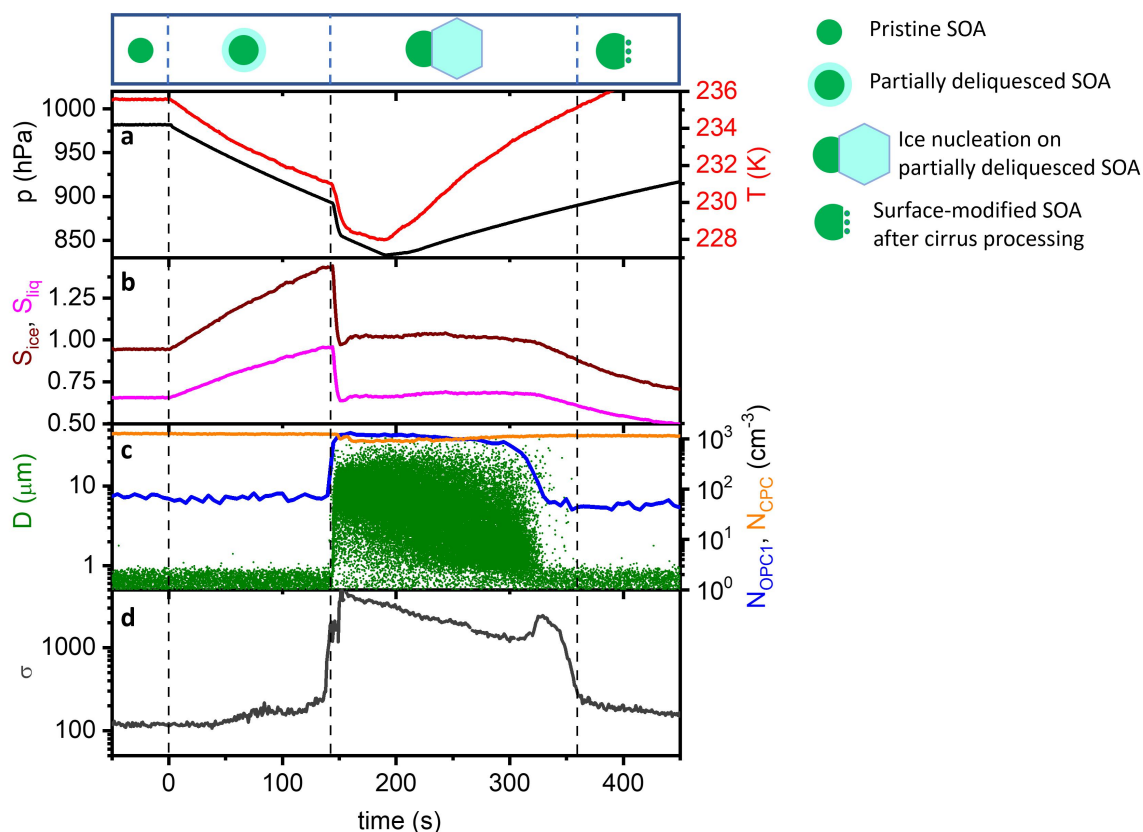


Figure 5.13: AIDA measurement data during the cirrus processing experiment with SOA particles generated from isoprene started at 235 K. The pictograms on top symbolize the various processing steps (see Fig. 5.3). The experimental time is given in seconds with respect to the start of pumping at time zero. The individual panels show the same types of measurement data as in Fig. 5.7.

crystals would then have grown quickly in the supersaturated environment, depleting the ice supersaturation and thereby prohibiting further ice formation on yet unactivated SOA particles. The consequence would have been fractional ice formation on only a subset of the aerosol population. The “super-expansion” guaranteed that the entire volume of the cloud chamber was suddenly cooled enough to cause ice formation. As can be seen in panel c, N_{OPC1} indeed closely matched N_{CPC} after the “super-expansion”, indicating ice formation on each SOA particle. Shortly afterwards, the pumping was stopped, and the ice crystals were sublimated by refilling the AIDA chamber to ambient pressure. The long-term trend of N_{OPC1} and σ in the time period after the cirrus processing, when the particles were sampled on filters for ESEM analysis, and their ice nucleation ability was measured with the CFDCs, is shown in Fig. 5.14.

The two “diagnostic” measurements for an immediate assessment of potential morphological changes in the particles, i.e., the N_{OPC1} -to- N_{CPC} ratio and σ , slightly changed from before to after cirrus processing. The N_{OPC1} -to- N_{CPC} ratio decreased from approximately 5.5 % before cirrus processing to 3.9 % afterwards, and σ increase by a factor of 1.2. These changes

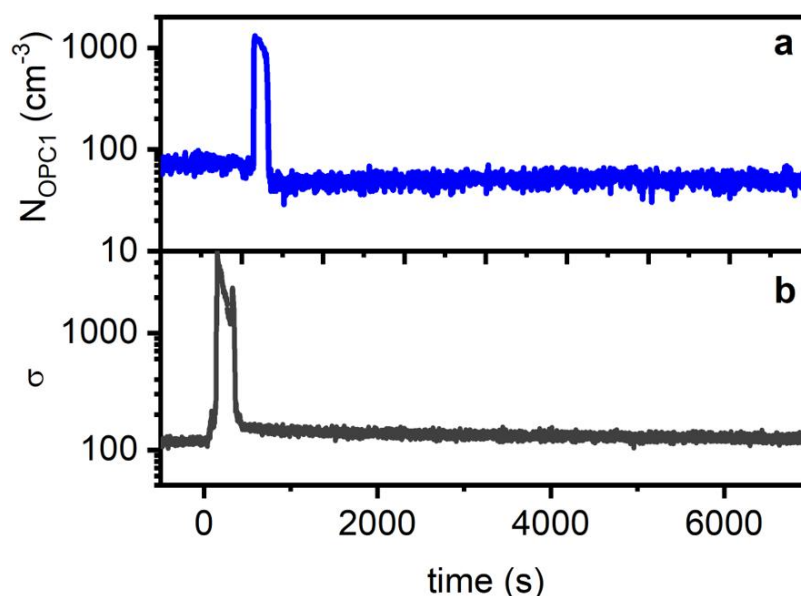


Figure 5.14: Long-term trend in the number concentration of $> 0.5 \mu\text{m}$ -sized particles measured by the OPC1 (N_{OPC1} , panel a) and the forward-to-backward scattering ratio σ (panel b) for the cirrus-processing experiment with isoprene-derived SOA particles started at 235 K.

are clearly smaller than those observed in the deep-convective cloud processing experiment. However, as already discussed in Section 5.1.2, it is expected that morphological changes will be smaller upon cirrus processing. These changes would presumably only affect the outer layers of the particle, rather than tearing the entire particle structure apart. This is exactly seen in the ESEM images, some representatives of which are shown in Fig. 5.15.

While the majority of the SOA particles processed in the cirrus updraft still have a compact shape, their outline has changed from strictly spherical to more bulbous or “potato-like”. This indeed speaks of a process similar to that sketched in scenario II of Fig. 5.3, in which partial deliquescence or liquefaction occurred during the AIDA expansion. A deformation of the spherical outline was then induced when the temporarily liquefied outer layer re-vitrified after ice nucleation and subsequent ice crystal sublimation. A different process is required to explain the ESEM picture at the bottom left. Perhaps the pristine particle had a lower viscosity than average, enabling the ice crystal to penetrate deeper and break it up.

A cirrus-processing experiment similar to that at 235 K was also conducted at 227 K. Here, the N_{OPC1} -to- N_{CPC} ratio and σ did not notably change in the process, and it can therefore be assumed that this experiment is representative of scenario I in Fig. 5.3. Unfortunately, due to time constraints, no ESEM analysis could be conducted for this experiment, and only the ice nucleation measurements taken before and after cirrus-processing are available. Dedicated re-compaction experiments, as performed after the simulations of deep-convective cloud

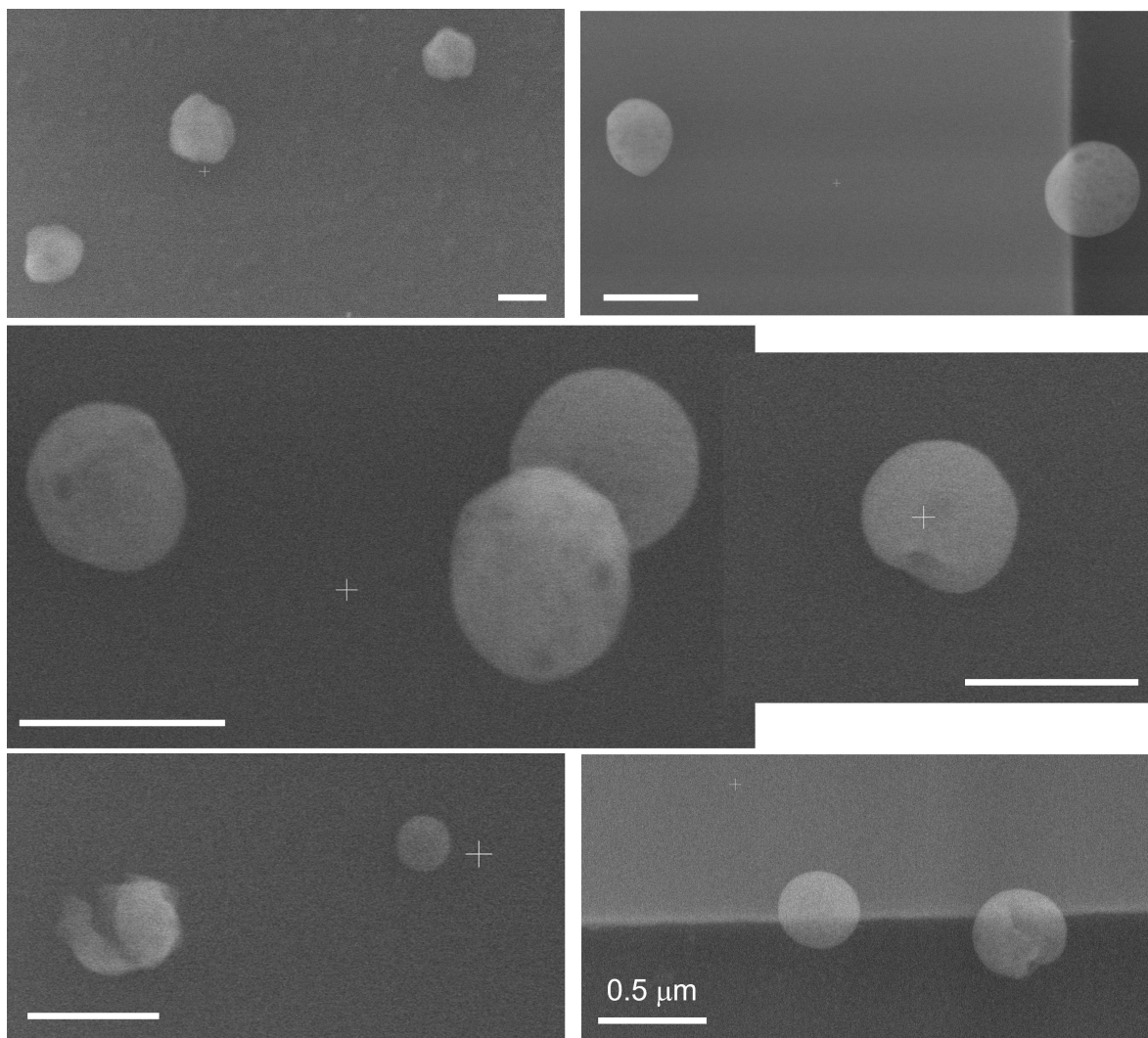


Figure 5.15: Representative ESEM images of isoprene-derived SOA particles collected from the AIDA chamber after the cirrus-processing experiment conducted at 235 K. Images are shown in different magnification with the white bar showing a length scale of 0.5 μm .

processing, were considered obsolete due to the only small morphological changes induced by cirrus-processing.

5.4.2 Change of the ice nucleation ability of the cirrus processed SOA particles

Fig. 5.16 shows the ice nucleation measurements for the isoprene-derived SOA particles with mINKA (part a, left) and INKA (part b, right) from the cirrus-processing experiment conducted at 235 K. The particles were sampled from the 235 K-cold AIDA chamber and the humidity ramps were conducted under cirrus conditions at temperatures of around 220 K. The color-coding of the AF vs. S_{ice} spectra again refers to the sampling periods or characterization stages: black lines correspond to the pristine SOA particles and red lines to the cirrus-processed

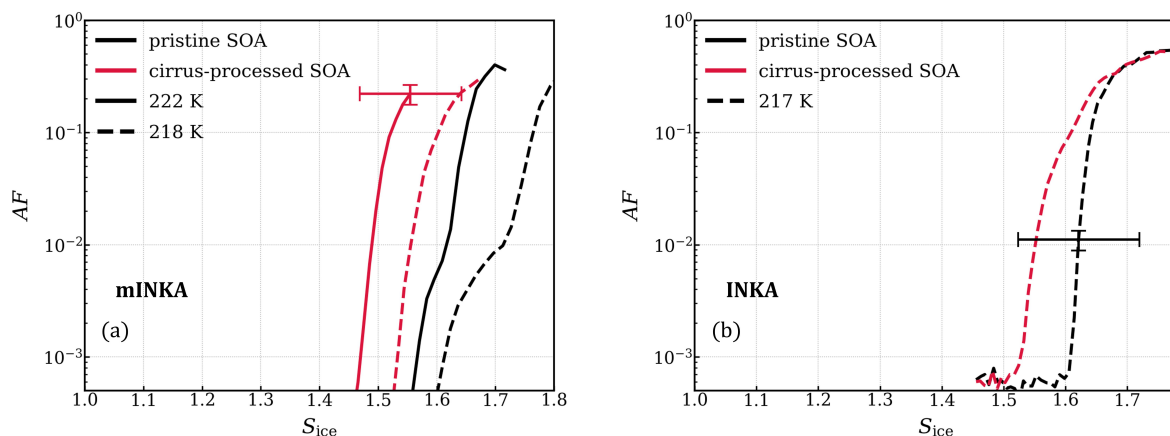


Figure 5.16: Ice nucleation measurements with mINKA (panel (a)) and INKA (panel (b)) during the cirrus-processing experiment with isoprene-derived SOA particles conducted at 235 K. The color coding refers to the different stages of the experiment (black: pristine particles, red: cirrus-processed particles). mINKA scans were conducted at two slightly different temperatures (solid and dashed lines), whereas INKA scans were only conducted at a single temperature. Horizontal and vertical error bars correspond to the uncertainties in the ice saturation ratio and the activated fraction (AF), respectively.

particles subjected to the expansion cooling experiment in the AIDA chamber. mINKA scans were conducted at two slightly different temperatures (solid and dashed lines), while INKA scans were only performed at a single temperature.

The CFDC data reveal a rather systematic shift of the AF spectra of the cirrus-processed SOA particles towards lower ice saturation ratios by an absolute amount of about 0.1 compared to the pristine SOA particles. In the left part of Fig. 5.17, the ice nucleation onsets extracted from Fig. 5.16 for an activated fraction of 0.1 % are shown in the S_{ice} vs. T diagram. The panel also includes the CFDC data from a second cirrus processing experiment at 235 K, which was conducted in the same way as that from Fig. 5.13. Again, one can only speculate about the small increase in the ice nucleation ability of the cloud-processed SOA particles.

In contrast to the deep-convective cloud processing, the improvement can hardly be explained by an increase in surface area, because the overall particle morphology remains rather compact after cloud processing. Occasionally, the cloud-processed particles reveal some cracks on their surface in the ESEM images, which could facilitate ice formation via the PCF mechanism. However, this cannot explain the shift of the AF spectra as a whole, i.e., for the entire aerosol population, towards lower ice saturation ratios. It is more reasonable to speak of a memory effect here, as the ice crystal has penetrated the organic matrix to some extent during the first nucleation event, possibly leaving an imprint that slightly lowered the nucleation barrier in the subsequent updraft. Nevertheless, the ice nucleation onsets of the cirrus-processed SOA particles are still very high, meaning that they are not efficient INPs. In the right part of Fig. 5.17, the ice nucleation onsets from the cirrus-processing experiment at 227 K are

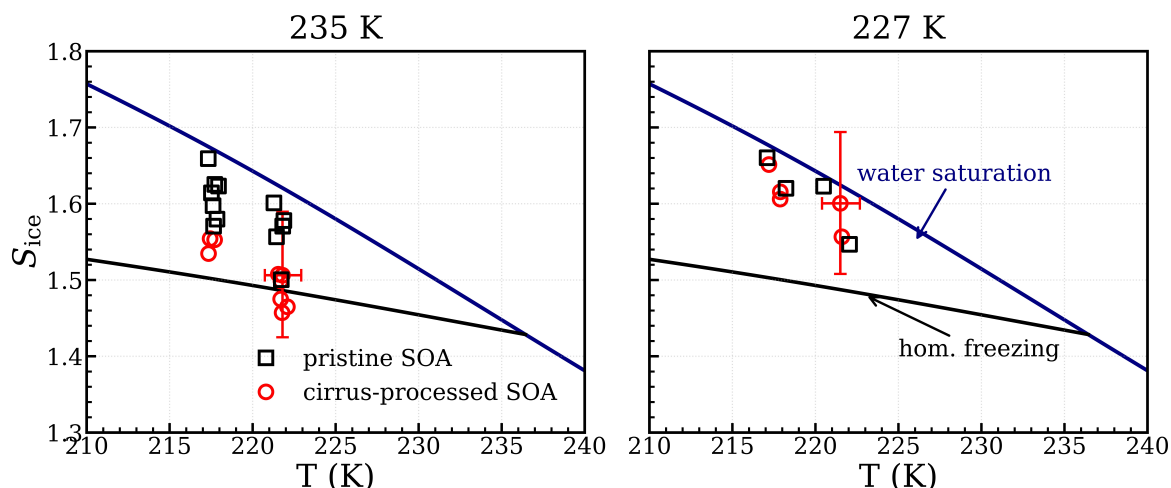


Figure 5.17: Temperature dependent onset conditions for ice formation by isoprene-derived SOA particles before (black squares) and after (red circles) cirrus processing at 235 K (panel (a), left) and at 227 K (panel (b), right). The black line denotes the threshold for the homogeneous freezing of aqueous solution droplets (Koop et al., 2000), and the blue line represents water-saturated conditions (Murphy et al., 2005).

shown. Intuitively, a lower temperature could harden the surface of the particles, making pre-activation by an ice “imprint” less likely. Indeed, the effect of cirrus processing at 227 K on the particles’ ice nucleation activity is negligible.

Overall, the results of this section are comparable to the data from the cirrus-processing experiments with α -pinene-derived SOA particles reported by Wagner et al. (2017) (see Fig. 5.5), showing that the effect of cirrus processing on the ice nucleation ability of SOA particles is very small, if not negligible. The new data suggest that pre-activation is slightly more efficient at warmer temperatures, where partial liquefaction in the first updraft is more likely to occur. This was not as clearly evident in the data of Wagner et al. (2017).

5.5 Summary and outlook

The new experiments conducted in this thesis, alongside those in the preceding studies by Wagner et al. (2017) and Wagner et al. (2024), have produced a consistent set of ice nucleation data for two different types of SOA precursors: isoprene and α -pinene. These results emphasize that various types of ice-cloud processing do not render pure SOA particles efficient INPs by inducing morphological changes. Despite a small decrease, the ice nucleation onsets after cloud-processing remain close to the conditions at which ubiquitous aqueous solution droplets would freeze anyway. Therefore, also the importance of cloud-processed, pure SOA particles in heterogeneous ice nucleation seems negligible. This means that the recommendation by Kasparoglu et al. (2022), which was based on a large set of measurements

for pristine SOA particles of different precursors, does not need to be revised, even if assuming that a certain fraction of particles undergo ice-cloud processing during their atmospheric lifetime. Of course, it is a matter of debate whether the new cloud processing experiments from this thesis, which use just one more SOA precursor, make this statement general enough, or whether further investigations are needed. Due to the difference in viscosity between α -pinene- and isoprene-derived SOM, it was possible to induce different degrees of morphological changes: the completely torn and fluffy structure in the case of α -pinene, compared to the more compact appearance in the case of isoprene. However, the results of the ice nucleation measurements were very similar.

Analyzing the static temperature and RH conditions under which porous particles can be stabilized, or the humidity threshold at which the porous particle structure collapses again, indicating the humidity-induced phase transition from the glassy into the liquid region, is an indirect way of investigating the viscous behavior of complex SOM at low temperatures, for which there is currently little measurement data available. While the potential effect on the particles' ice nucleation ability might be small, further freeze-drying experiments with pure SOA particles could allow changes in the viscosity of complex SOM at low temperatures to be investigated systematically, depending on factors such as oxidation conditions or exposure to UV solar light (Baboomian et al., 2022).

The isoprene experiments described here were among the last conducted in the classic AIDA chamber before it was decommissioned. Another important issue, which was investigated by Wagner et al. (2024), could therefore not yet be addressed due to limited time availability and must be resumed when AIDA's planned successor is ready. This addresses the situation in which the SOM is not present as a pure SOA particle, but is mixed internally and forms, for example, a coating layer on mineral dust. The experiment described in Section 4.4.3 shows that a coating layer of this kind completely deactivates the intrinsic ice nucleation ability of dust, which is consistent with previous studies, and led Kasparoglu et al. (2022) to include such coated dust particles in the category of ice-inactive particles. However, Wagner et al. (2024) showed that, in the case of a dust particle coated with SOM, deep-convective cloud cycling could provoke a much larger change in ice nucleation ability than in the case of pure SOA particles. This is because the initially compact coating layer of organic matter can be partially torn away from the dust surface. This re-exposes the active sites on the dust, meaning that such cloud-processed particles are no longer ice-inactive. In the future, it would be highly valuable to confirm these results with another set of experiments using dust particles coated with SOM from isoprene oxidation in the Aerosol Interaction and Dynamics in the Atmosphere cold and clean (AIDA_{c2}) chamber.

From an experimental point of view, the AIDA chamber has been useful for this study, despite its limitations in terms of the dynamic temperature range, especially when used

alongside CFDCs. Similar to the coating experiments presented in Chapter 4, AIDA was used as a reactor and reservoir tank to generate and stabilize the porous particles over a long period of time, while carrying out filter sampling for the ESEM analysis and ice nucleation measurements with the CFDCs. This should be similarly feasible with the AIDA chamber's successor. An alternative approach would be to use the dynamic AIDA cloud chamber (AIDAd) with its actively coolable inner walls (Alpert et al., 2023). The extended dynamic temperature range would allow the simulation of deep-convective cloud cycling to be more realistic. However, although freeze-dried SOA particles can in principle be released into a cold atmosphere down to -50°C in AIDAd chamber, this temperature cannot be maintained for extended periods due to the limited available volume of precooled oil circulated through the chamber walls. Higher time resolution and more rapid measurements of ice nucleation under cirrus conditions are then needed, such as those provided by new developments in the Portable Ice Nucleation Experiment (PINE) family (Bogert, 2024).

6 Chemical aging of sulfate-containing seed aerosol particles

This chapter investigates whether chemically driven atmospheric aging alters the ice nucleation efficiency of atmospherically relevant aerosol particles. In particular, it focuses on the reactive uptake of gas-phase organic precursors and the subsequent formation of secondary organic material (SOM) on sulfate-containing seed particles. Such processes can modify aerosol composition, surface chemistry, water content, morphology, and phase state, and may therefore influence the particles' ice nucleation ability. However, compared to the physical aging pathways discussed in Chapter 4, chemically driven aging processes have so far received less attention in the context of cirrus formation.

In order to address this knowledge gap, this chapter compares two types of chemically modified sulfate seed aerosol particles: those coated with isoprene-derived SOM, and those chemically aged through glyoxal uptake. The seed particles were either pure sulfuric acid solution droplets or crystalline ammonium sulfate particles, resulting in a matrix of four individual experiments. The experiments were conducted at the European Organization for Nuclear Research (CERN) Cosmics Leaving Outdoor Droplets (CLOUD) facility, which enables detailed gas- and particle-phase chemical characterization under controlled chamber conditions. In these experiments, the CLOUD chamber served as the reaction chamber, while the mobile Continuous Flow Diffusion Chamber (CFDC) mINKA was used to continuously monitor the ice nucleation activity of the processed aerosol particles.

Chapter 6 is structured as follows. Section 6.1 introduces the relevance of sulfate aerosol particles in the atmosphere, their interactions with organic compounds, and how they can be chemically modified through reactive uptake. It then reviews previous ice nucleation studies involving chemically complex sulfate particles, identifying the limitations that motivated the present study. Section 6.2 describes the experimental procedure, emphasizing how the use of a combination of mass spectrometers, particle counters, the CLOUD chamber, and mINKA allows for the simultaneous characterization of both the chemical aging of aerosol particles and their ice nucleation activity. Section 6.3 presents the ice nucleation results for the two experiments involving acidic seed particles: sulfuric acid–glyoxal and sulfuric acid–isoprene. The corresponding two experiments with crystalline ammonium sulfate seed aerosol particles are detailed in Section 6.4. Finally, Section 6.5 summarizes the main findings and discusses implications for ice cloud formation.

6.1 Background

6.1.1 Chemical complexity of sulfate aerosol particles – field measurements

Sulfuric acid solution droplets are produced in the atmosphere from the oxidation of sulfur dioxide, SO₂, which comes from both natural sources, such as volcanic eruptions, and from anthropogenic emissions linked to industrial activity. These aerosol particles are widespread and are especially important in the Upper Troposphere Lower Stratosphere (UTLS), where the aerosol chemical composition is dominated by sulfuric acid solution droplets. However, such sulfate-containing particles in the UTLS are often chemically complex. They can react with organic compounds to form organosulfates, be neutralized by ammonia or amines, or undergo other chemical transformations. For example, internal mixtures of neutralized sulfate with organic material were identified by single particle mass spectrometry as the dominant particle class of subvisible cirrus residuals (Froyd et al., 2010).

The chemical complexity of sulfate aerosol particles is particularly evident in the Asian Tropopause Aerosol Layer (ATAL). Airborne observations in the UTLS have shown a strong presence of organosulfates, indicating that ATAL particles are mixtures of secondary organic and inorganic components (Appel et al., 2022). In the ATAL, organosulfates are often internally mixed with ammonium and nitrate. Single particle mass spectrometry has shown that mixtures of nitrate, ammonium, sulfate, and organic matter dominate the aerosol population. These results suggest that ATAL aerosol particles are formed through several processes, including new particle formation, coagulation, condensational growth, convective transport, and scavenging, rather than by new particle formation alone (Mahnke et al., 2021; Weigel et al., 2021).

Long-term airborne measurements also support this view. Martinsson et al. (2019) found an increasing co-presence of carbon-, sulfate-, and oxygen-containing compounds in UTLS aerosol particles, even without volcanic influence. These studies show that sulfate-containing aerosol particles in the upper troposphere are abundant and chemically mixed. Their formation depends on suitable chemical conditions. For example, oxidation of monoterpenes in the presence of acidic sulfate seed particles can promote organosulfate formation (Surratt et al., 2008).

Mixed organic–sulfate aerosol particles are also important outside the UTLS. Ground-based and shipborne measurements show that organic-rich outflow from South Asia changes chemically during transport and becomes more sulfate-rich over the Northern Indian Ocean (Hegde et al., 2022; Nair et al., 2023). During strong continental outflow, non-sea salt sulfate concentrations increased by more than a factor of two (Aswini et al., 2020). The same air masses also showed elevated particulate organic concentrations (Kompalli et al., 2020).

6.1.2 Reactive uptake of organic precursors on sulfate aerosol particles

The reactive uptake of gas-phase precursors is an important process through which sulfate-containing seed particles undergo chemical aging to exhibit the compositional complexity discussed above. The potential reaction pathways depend on the acidity of the seed particles. Acidic sulfuric acid solution droplets promote heterogeneous reactions and acid-catalyzed processes such as oligomerization and organosulfate formation. In the presence of ammonia, additional reaction pathways become possible. For example, ammonia can react with oxidized organic compounds in acidic particles and form organonitrogen species (Nozière et al., 2009).

Glyoxal is one of the most important precursors involved in this type of chemistry. It is highly reactive in aqueous aerosol particles and can form low-volatility products. Liggio et al. (2005a) showed that glyoxal uptake onto particles can produce acetals and sulfate esters, leading to rapid and sustained particle growth under atmospherically relevant conditions. Other laboratory studies have shown that acidic sulfate particles can take up several organic vapors at the same time. The uptake of compounds such as glyoxal and pinanediol depends strongly on particle acidity and relative humidity (RH), showing that both aerosol composition and environmental conditions control reactive uptake (Liggio et al., 2005b; Qin et al., 2020).

Inside aqueous particles, glyoxal can react with ammonia through nucleophilic addition to its carbonyl groups. This reaction forms carbinolamine intermediates, which can dehydrate to form imines. Further reactions can then produce imidazole and substituted imidazole compounds, especially at high ammonium concentrations (Amugoda et al., 2025). These reactions are important because they convert volatile or semi-volatile precursors into low-volatility organonitrogen and oligomeric products. As a result, they contribute to particle growth and chemical aging (Hamilton et al., 2013; Marracci et al., 2025).

Recent theoretical work also shows that sulfuric acid and ammonia can enhance each other's role in glyoxal chemistry. Lin et al. (2023) showed that NH_3 promotes gas phase glyoxal + H_2SO_4 reactions, while H_2SO_4 strongly catalyzes glyoxal + NH_3 reactions. This suggests that carbinolamine formation may compete with OH loss of glyoxal under atmospheric conditions. However, reactive uptake does not only depend only on the gas-phase precursor. It also depends on the chemical and physical properties of the seed particle. For example, nonanal shows limited uptake onto pure sulfuric acid solution droplets, but its reactivity increases when particle-phase organics are present (Chan et al., 2011). This shows that a mixed aerosol composition can favor heterogeneous chemistry.

The particles' phase state is another important factor in determining reactive uptake. Deliquesced ammonium sulfate particles usually show stronger uptake than solid particles because liquid water allows reactions to occur both at the surface and within the particle bulk (Brun et al., 2025). Glyoxal uptake onto ammonium-containing salts also depends on RH and dissolved salt concentration. At high ionic strength, water activity decreases, which can

reduce glyoxal solubility in the aqueous phase through a salting-out effect (Gen et al., 2018). Glyoxal uptake, however, has also been observed at low RH, such as 26 % RH (Hastings et al., 2005). Together, these studies show that particle water content, ionic strength, and phase state influence both the amount of uptake and the nature of the reaction products that are formed (Kroll et al., 2005).

Similar processes are important for other organic precursors. The uptake of isoprene oxidation products depends on their vapor pressure, their solubility in aqueous particles, and their ability to undergo condensed-phase reactions. Including such processes in aerosol models improves agreement with chamber experiments, especially when oligomerization reactions are taken into account (Couvidat et al., 2018). Laboratory studies also show that pinonaldehyde can be taken up by acidic sulfate aerosol particles through acid-catalyzed reactions, forming particle-phase products and contributing to progressive aerosol aging (Liggio et al., 2006).

Overall, reactive uptake transforms pristine sulfuric acid or ammonium sulfate seed particles into chemically mixed organic–inorganic particles. This transformation changes not only particle composition but also physical properties such as water content, viscosity, and phase state. The formation of oligomers and imidazole-type compounds can increase molecular weight and strengthen hydrogen-bonding networks, making particles more viscous or even semi-solid. Dehydration reactions can further lower water activity and reinforce these changes. As chemically aged particles become more viscous or develop core-shell structures, the accessibility of surface functional groups and interfacial properties may also change. These particle modifications in terms of composition, water content, and phase state, which are induced by the reactive uptake, may ultimately alter the ice nucleation behavior compared to the pristine seed particles. Therefore, reactive uptake provides a direct link between sulfate aerosol chemistry and ice nucleation behavior because it controls the chemical mixing state and phase state of the seed particles.

6.1.3 Earlier studies on the ice nucleation behavior of chemically mixed sulfate particles

Despite their abundance, the role of chemically mixed, sulfate-containing aerosol particles in ice cloud formation is still not extensively studied. The pristine particle types sulfuric acid and ammonium sulfate are well characterized regarding their ice nucleation behavior under cirrus conditions. While sulfuric acid solution droplets freeze homogeneously (Koop et al., 2000; Schneider et al., 2021), crystallized ammonium sulfate particles, as discussed previously in Chapter 4, allow for heterogeneous ice formation. In a recent series of systematic Aerosol Interaction and Dynamics in the Atmosphere (AIDA) experiments, a parameterization was derived to quantitatively describe not only the ice nucleation ability of fully ammoniated

(NH₄)₂SO₄ particles, but also that of partially neutralized particles, such as crystalline mixtures of letovicite, (NH₄)₃H(SO₄)₂, and ammonium bisulfate, NH₄HSO₄ (Bertozzi et al., 2024).

Recent studies have examined the ice nucleation activity of organosulfates, including field observations by Wolf et al. (2020) and laboratory measurements by Rapp et al. (2025). The field measurements by Wolf et al. (2020) suggest that organosulfates from isoprene emissions can induce heterogeneous ice nucleation, but the significance of these observations is limited by the very low ice-active fractions measured using the deployed CFDC. The laboratory-based CFDC measurements of methyl-, ethyl-, and dodecyl-organosulfates showed no evidence of heterogeneous ice nucleation activity. This is possibly because these proxy compounds have low glass transition temperatures (Rapp et al., 2025). The authors speculated that a greater number of functional groups (e.g., hydroxyl, carboxyl, hydroperoxyl, and carbonyl) in “real” atmospheric organosulfates compared to their proxy compounds could raise the glass transition temperature, enabling a heterogeneous ice nucleation mode. In summary, these two studies did not directly assess how chemical aging alters the ice nucleation behavior. Instead, they either relied on proxy compounds for organosulfates or inferred relationships between ambient organosulfate concentrations and ice crystal number concentrations. Thus, while they indicate that organosulfate-containing particles may be relevant for heterogeneous ice formation, they do not resolve how aging processes modify the ice nucleation ability of mixed organic–sulfate particles.

Furthermore, a couple of ice nucleation studies are available for mixtures of ammonium sulfate and organics. The condensation of the reaction products from the ozonolysis of α -pinene onto crystalline ammonium sulfate particles led to a highly viscous or glassy coating layer that completely shielded the intrinsic heterogeneous ice nucleation ability of the seed particles (Bertozzi et al., 2021). The heterogeneous ice nucleation ability of the crystalline seeds may be retained in the case of incomplete coatings (Wise et al., 2010), or it may be “restored” if the coating layer is morphologically modified to a porous structure through ice-cloud processing (see also Chapter 5) (Bertozzi et al., 2021). When embedded in liquid organic matrices, immersion freezing of solid “islands” of ammonium sulfate becomes a potential heterogeneous ice nucleation pathway (Lei et al., 2023; Schill et al., 2014). But these ice nucleation studies do not directly probe the impact of chemically driven aging in mixtures containing organics, sulfuric acid, and ammonium. In particular, the ways in which acid–base chemistry, neutralization, and organosulfate formation alter particle structure and influence heterogeneous ice nucleation remain unclear.

6.1.4 Motivation, objectives, and scope of this study

The preceding discussion has shown that sulfate-containing aerosol particles are atmospherically abundant, chemically complex, and frequently internally mixed with organic material.

Reactive uptake and condensed-phase chemistry can substantially modify particle composition, phase state, and morphology, all of which are closely linked to the particles' ice nucleation behavior. Nevertheless, the extent to which chemical aging affects the ice nucleation ability of mixed organic–sulfate aerosol particles remains poorly constrained.

Among these processes, glyoxal-derived formation of SOM is particularly relevant. Unlike many SOM formation pathways that are governed largely by equilibrium gas-particle partitioning, glyoxal SOM formation is driven primarily by reactive uptake and aqueous-phase chemistry in the condensed phase (Volkamer et al., 2007). Therefore, glyoxal provides a useful model system for investigating how heterogeneous and multiphase chemistry shape aerosol composition, chemical aging, and physicochemical properties. Because these properties influence phase state, morphology, and freezing behavior, glyoxal-driven chemical aging offers a suitable framework for examining how chemical processing modifies the ice nucleation efficiency of organic–sulfate aerosol systems.

In the framework of this thesis, the reactive uptake of glyoxal on two different types of seed particles, aqueous sulfuric acid solution droplets and crystalline ammonium sulfate, was investigated for the first time in conjunction with the evolution of the particles' ice nucleation ability under cirrus conditions. The experiments described in this chapter were conducted at the CERN CLOUD facility during the CLOUD17 campaign in autumn 2024. This facility enables the investigation of aerosol particle formation and evolution under clean, highly controlled chamber conditions using a suite of mass spectrometers (for gas and particle phase) and particle counters. These measurements were complemented here with continuous ice nucleation measurements using the mobile CFDC instrument mINKA. For the purpose of comparison, the two glyoxal experiments were supplemented with two equivalent experiments with a different SOM precursor, namely isoprene.

6.2 Experimental procedure

The general setup of the CERN CLOUD chamber and the measurement techniques employed have already been introduced in Section 3.2.2. This section provides a brief summary of the experimental timeline.

Throughout the experiments, the CLOUD chamber was maintained at approximately 241 K and conditioned to a S_{liq} of around 0.3 (S_{ice} of about 0.41). Humidity scans using mINKA were conducted at 223 K in the cirrus regime to investigate the ice nucleation ability of the processed aerosol particles.

As described in Section 3.2.2, the newly developed FLOW Tube System (FLOTUS) system was used to generate aqueous sulfuric acid solution droplets with a median diameter of about 130 nm, which were then transferred into the CLOUD chamber through the gate valve (GV).

In two experiments, these acidic solution droplets were used directly for chemical processing with either glyoxal or isoprene. In two other experiments, processing began after the in situ neutralization of the sulfuric acid solution droplets into ammonium sulfate by adding excess ammonia to the CLOUD chamber. As the chamber was conditioned below the RH at which ammonium sulfate effloresces, crystallization of the aerosol particles is expected, as has been observed by means of infrared extinction spectroscopy and depolarization measurements in similar experiments previously conducted at the AIDA chamber (Bertozzi et al., 2024). While such instrumentation was unavailable at the CLOUD chamber to directly prove the crystalline nature of the seed particles, crystallization could be indirectly confirmed by the appearance of a heterogeneous ice nucleation mode in the mINKA scans after neutralization. This can only be explained by the presence of solid particles.

Once a sufficient number and mass concentration of seed aerosol particles had been reached, the continuous supply of ozone, together with either glyoxal or isoprene as organic precursors, was initiated to instigate the chemical aging process. Aging was first conducted for a certain time period “in the dark”, without illumination. Afterwards, selected low-pressure mercury (Hg) lamps from the UV illumination system of the CLOUD chamber were switched on to photolyze ozone at 254 nm and generate OH radicals, thereby accelerating the chemical processing. Throughout the aging process, the aerosol population was characterized by size distribution measurements, ice nucleation measurements, and mass spectrometric analyses. Further particular details of the experimental procedure are discussed below. After each experiment, the CLOUD chamber was cleaned by operating the fans at 100 % efficiency and applying high voltage to remove residual particles.

6.3 Ice nucleation behavior of sulfuric acid–organic mixtures

6.3.1 Ice nucleation behavior of the sulfuric acid–glyoxal mixture

Fig. 6.1 shows a compilation of the relevant measurement data for the aging experiment with the sulfuric acid–glyoxal mixture. The timeline starts with the injection period of sulfuric acid solution droplets from FLOTUS into the CLOUD chamber, which was maintained at 241 K and S_{liq} of around 0.3 (S_{ice} of about 0.41). At the beginning of the experiment, the ozone concentration was approximately 85 ppb. After an initial mINKA humidity scan with the pure sulfuric acid solution droplets, the injection of glyoxal into the chamber was started (18:58 UTC). Additional mINKA scans were then performed to follow the evolution of the ice nucleation ability alongside changes in the aerosol chemical composition.

Panel (a) of Fig. 6.1 shows the concentration of glyoxal in the gas phase, which was kept at around 1.85 ppb during the aging period. Panel (b) shows the organic-to-sulfate mass ratio of the aerosol particles, as derived from the high-resolution time-of-flight Aerosol Mass

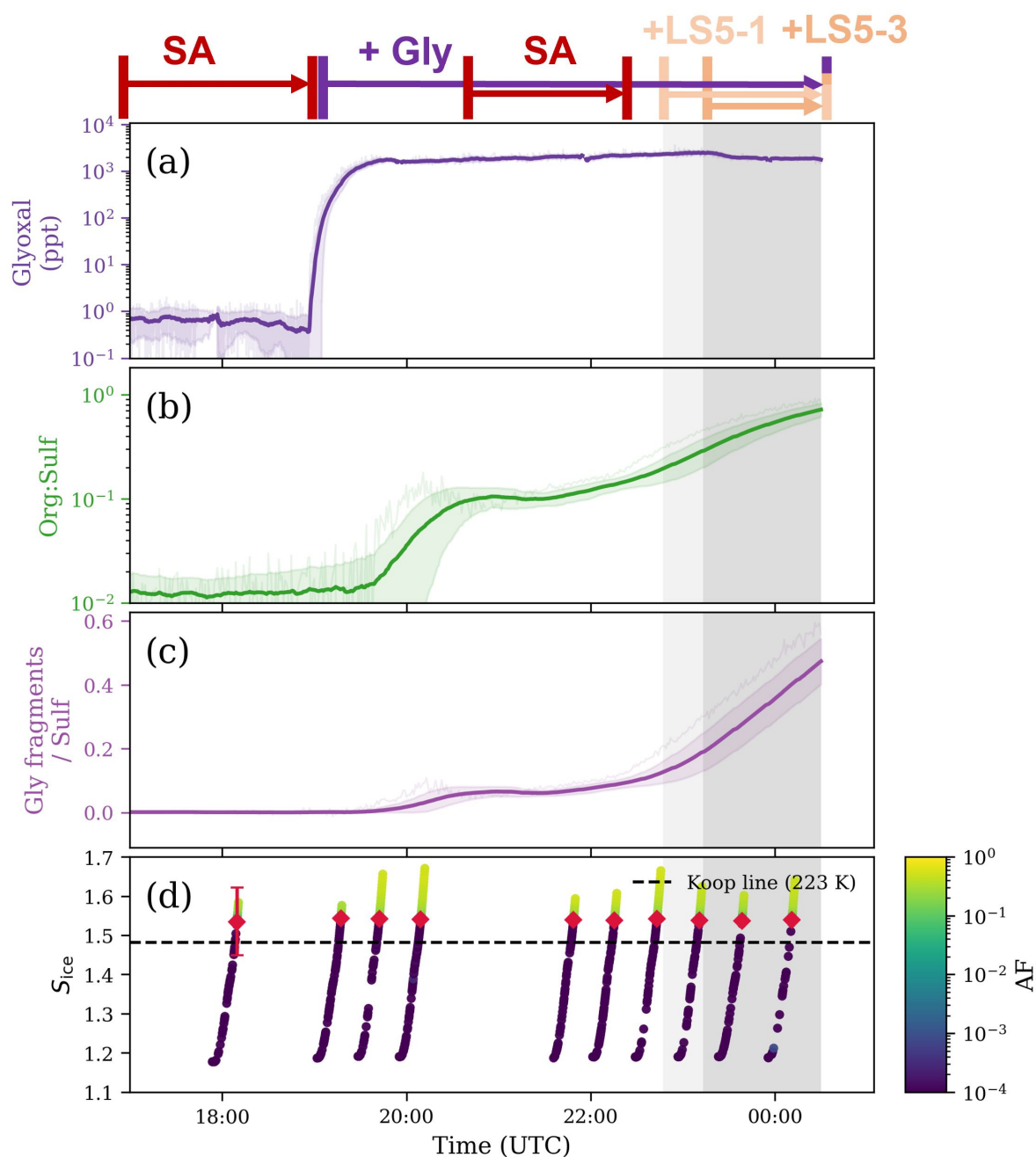


Figure 6.1: The sulfuric acid-glyoxal aging experiment. Panel (a): Concentration of glyoxal in the gas phase; panel (b): organic-to-sulfate mass ratio of the aerosol particles; panel (c): concentration of glyoxal-related particle fragments, normalized to the sulfate mass concentration; panel (d): trajectories of the ice nucleation measurements with mINKA throughout the aging process, using color coding to denote the ice-active fraction of the particle population. Red diamonds indicate an activated fraction (AF) of 0.1 %. The dashed black line corresponds to the homogeneous ice nucleation threshold based on the water-activity criterion described by Koop et al. (2000). The top legend depicts the experimental procedure, with periods of irradiation with lamps 1 and 3 of the LS5 system additionally highlighted by shaded regions.

Spectrometer (HR-ToF-AMS). Panel (c) shows the concentration of glyoxal-related particle fragments, normalized to the sulfate mass concentration. The shaded regions indicate periods of irradiation using lamp 1 of the LS5 system, followed by irradiation using lamps 1 and 3 of LS5 together. As the seed aerosol particle concentration had decreased substantially by this stage of the experiment due to wall and sampling losses, an additional injection of sulfuric acid solution droplets from FLOTUS was performed, as indicated in the top legend of Fig. 6.1.

When glyoxal was added to the chamber containing the sulfuric acid seed aerosol particles, a slight increase in the amount of organic material in the particle phase was observed. The presence of glyoxal-related particle fragments in the HR-ToF-AMS measurements indicates that the sulfuric acid solution droplets have taken up glyoxal. This uptake was weak under dark conditions but increased during UV irradiation due to the formation of condensable oxidation products, as reflected by the enhanced abundance of glyoxal-related fragments in the later periods of the experiment. OH-radical-driven glyoxal chemistry also manifested itself in an order-of-magnitude increase in gas-phase concentrations of $C_2H_2O_5$, $C_2H_2O_6$, C_2HO_8N , and $C_4H_6O_2$ during irradiation (Nitrate-CI-API-TOF, data not shown).

Despite these compositional changes, the ice nucleation ability of the seed aerosol particles remained virtually unchanged during aging, as indicated by the series of mobile Ice Nucleation instrument of the Karlsruhe Institute of Technology (mINKA) humidity scans shown in Fig. 6.1, panel (d). The pristine sulfuric acid solution droplets nucleated ice at (or slightly above) the homogeneous freezing threshold, as did the mixed sulfate-organic particles after the uptake of glyoxal and its oxidation products. This suggests that the particles likely remained low-viscosity droplets with a sufficiently low glass transition temperature in order to exhibit a freezing behavior similar to that of pure sulfuric acid solution droplets.

6.3.2 Ice nucleation behavior of the sulfuric acid–isoprene mixture

A similar experiment to the one described in Section 6.3.1 was performed using isoprene as the organic precursor, as shown in Fig. 6.2. The isoprene addition to the chamber containing the sulfuric acid solution droplets was started at 21:00 UTC. Only a very subtle increase in the organic-to-sulfate ratio was observed under dark conditions, suggesting that the uptake of organic material into the particle phase was negligible. In contrast, irradiation with LS5 lamp 1 at around 22:07 UTC led to a gradual increase in the organic-to-sulfate ratio. The organic-to-sulfate ratio increased further after LS5 lamp 3 was switched on at 22:36 UTC, indicating enhanced formation and uptake of oxidized organic material in the particle phase.

Despite these compositional changes, no appreciable change in the ice nucleation behavior was observed, as shown in panel (c), Fig. 6.2. The particles continued to nucleate ice at high ice saturation ratios slightly above the homogeneous freezing threshold. Therefore, the addition of isoprene or the photochemical formation of isoprene-derived organic material did

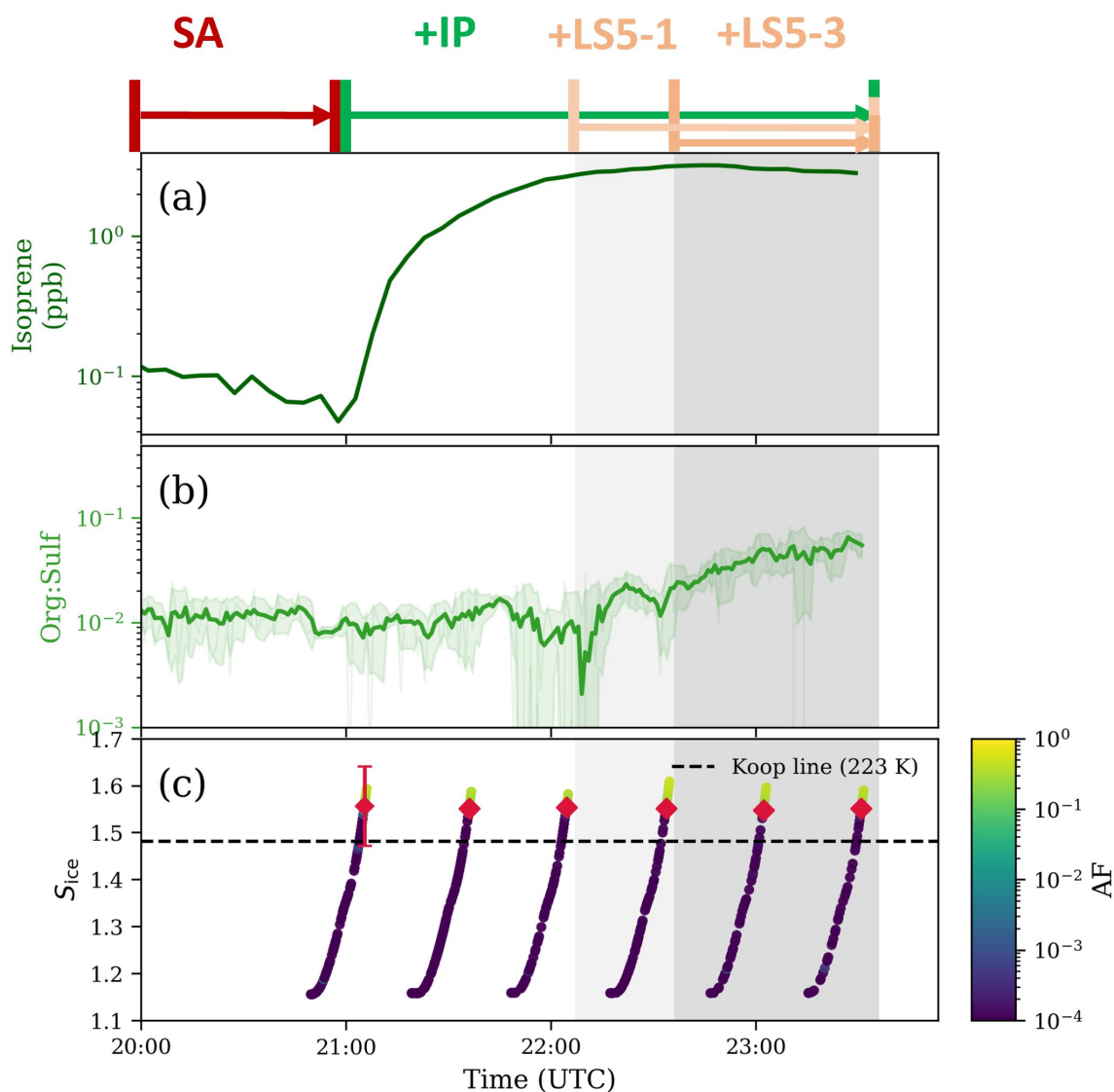


Figure 6.2: The sulfuric acid-isoprene aging experiment. Panel (a): Concentration of isoprene in the gas phase; panel (b): organic-to-sulfate mass ratio of the aerosol particles; panel (c): trajectories of the ice nucleation measurements with mINKA throughout the aging process, using color coding to denote the ice-active fraction of the particle population. Red diamonds indicate an AF of 0.1 %. The dashed black line corresponds to the homogeneous ice nucleation threshold based on the water-activity criterion described by Koop et al. (2000). The top legend depicts the experimental procedure, with periods of irradiation with lamps 1 and 3 of the LS5 system additionally highlighted by shaded regions.

not lead to the appearance of a heterogeneous ice nucleation mode for the chemically aged sulfuric acid seed aerosol particles. This suggests that either no crystalline compounds were formed, or the glass transition temperature of the particles was not increased enough to turn the aqueous solution droplets into highly viscous particles.

In summary, the chemical aging of the acidic seed aerosol particles with the two different types of organic precursors had an insignificant impact on their ice nucleation behavior. The next section will explore the outcomes of the chemical processing experiments when the aqueous sulfuric acid solution droplets were neutralized by ammonia, yielding crystalline ammonium sulfate seed particles. Note that this alters the starting point of the experiments. Rather than starting with a homogeneous freezing mode, the seed particles now already have an intrinsic heterogeneous ice nucleation ability, which can be enhanced or deactivated through chemical processing.

6.4 Ice nucleation behavior of ammonium sulfate–organic mixtures

6.4.1 Ice nucleation behavior of the ammonium sulfate–glyoxal mixture

Fig. 6.3 shows a compilation of relevant measurement data for the gas and particle phase composition during the aging experiment with the ammonium sulfate–glyoxal mixture. Note that the concomitant ice nucleation measurements will be shown later in a separate figure. The appendix contains an additional figure showing other basic chamber data throughout the experiment (Fig. A.2).

The timeline of the experiment again starts with the injection period of sulfuric acid solution droplets from FLOTUS into the CLOUD chamber, which was maintained at 241 K and S_{liq} of around 0.3 (S_{ice} of about 0.41). As shown by the HR-ToF-AMS mass concentration measurements in Fig. 6.3 (b), this injection led to an increase in not only the sulfate but also the ammonium concentration, even before the deliberate addition of ammonia to the chamber was started at 11:11 UTC. This is due to an inherent background concentration of NH_3 from previous CLOUD experiments. The injection of sulfuric acid droplets was stopped shortly after glyoxal was introduced, while the continuous supply of ammonia was maintained in order to preserve a neutralized aerosol population and have some excess of ammonia in the gas phase. At the end of the sulfuric acid addition, the particle composition was indeed dominated by the fully neutralized salt, that is $(\text{NH}_4)_2\text{SO}_4$ (Fig. 6.3 (c), dashed orange line).

The glyoxal addition was started at 13:19 UTC (Fig. 6.3 (a)). The HR-ToF-AMS measurements show a clear increase in particle-phase organic material immediately after the start of glyoxal injection (Fig. 6.3 (b), dashed green line). In contrast to the sulfuric acid–glyoxal experiment, the organic-to-sulfate ratio increased substantially even under dark conditions (Fig. 6.3 (c), brown line). This indicates that efficient glyoxal uptake did not require irradiation, but was likely promoted by reactions with ammonium-containing particle-phase components. Therefore, the observed behavior is more consistent with reactive uptake, followed by the formation of condensed-phase products with lower volatility, than with simple, reversible

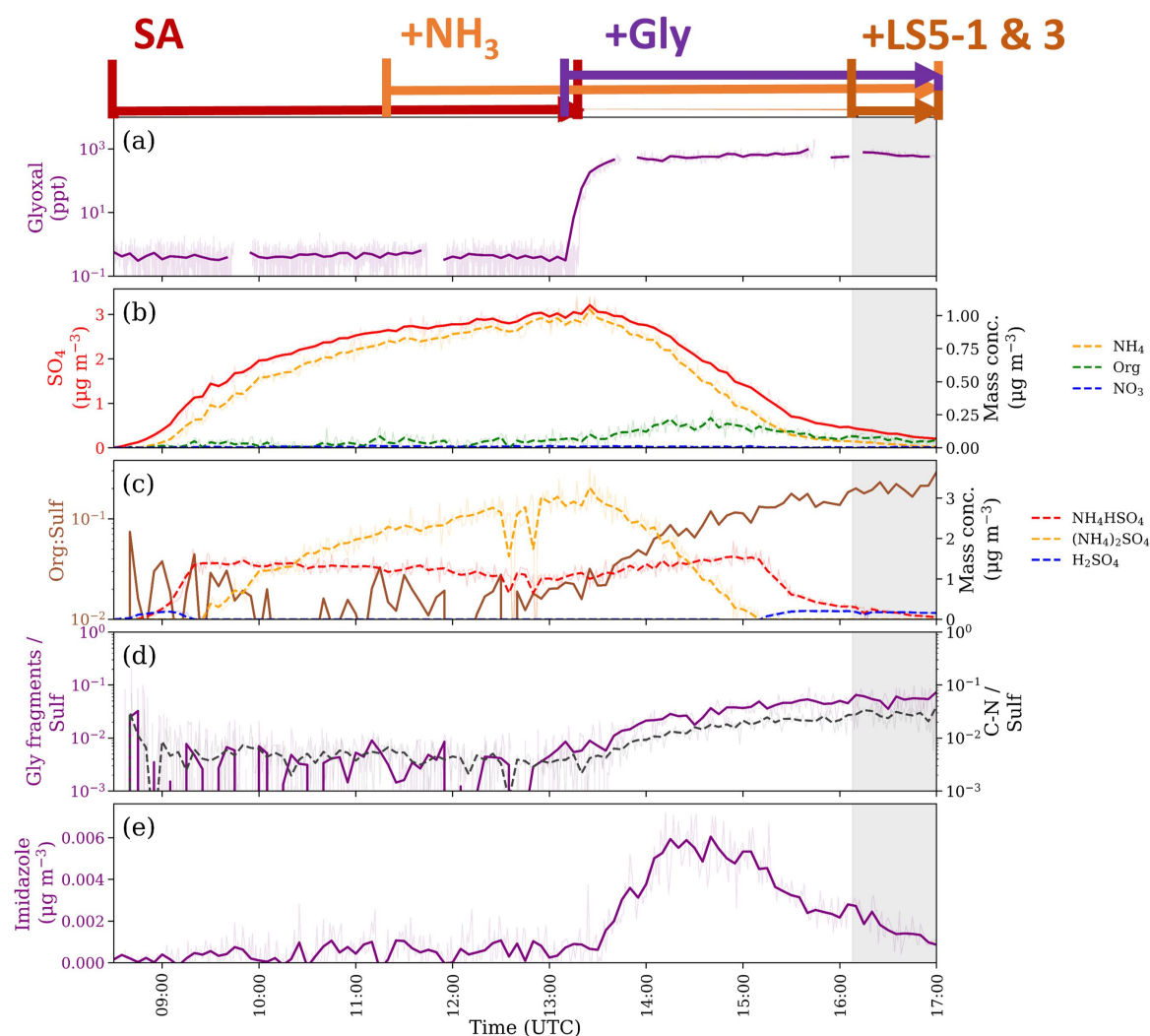


Figure 6.3: Gas- and particle-phase composition during the ammonium sulfate–glyoxal aging experiment. The experimental timeline is depicted on top, with the additional shading indicating the period of irradiation with LS5 lamps 1 and 3. In all panels, solid lines correspond to the scaling on the left axes, whereas dashed lines correspond to the right axes. Panel (a): temporal evolution of the gas-phase concentration of glyoxal. Panel (b): HR-ToF-AMS-derived mass concentrations of sulfate (left axis) as well as ammonium, organics, and nitrate (right axis). Panel (c): organic-to-sulfate mass ratio (left axis) and estimated mass concentrations of ammonium sulfate, ammonium bisulfate, and sulfuric acid (right axis). Panel (d): ratio of glyoxal-related fragments to sulfate (left axis) and ratio of C–N-containing fragments to sulfate (right axis). Panel (e): imidazole concentration retrieved from the HR-ToF-AMS measurements.

gas–particle partitioning alone (Galloway et al., 2009; Kampf et al., 2012; Kroll et al., 2005; Nozière et al., 2009).

Further evidence for particle-phase chemical processing is provided by the increase in nitrogen-containing organic fragments (C–N, Fig. 6.3 (d), dashed black line) and by the

appearance of imidazole-related compounds (Fig. 6.3 (e)). These products are consistent with reactions between glyoxal and ammonium-containing aerosol components. As already indicated in Section 6.1.2, glyoxal is known to form SOM through reactive uptake, aqueous-phase oxidation, oligomerization, and the formation of low-volatility products (Ervens et al., 2011; Knote et al., 2014; Liggio et al., 2005b; Nozière et al., 2009; Volkamer et al., 2009). In ammonium-containing aerosol particles, glyoxal can additionally react through carbonyl–nitrogen pathways, producing organonitrogen compounds such as imidazole-related species (Galloway et al., 2009; Kampf et al., 2012; Nozière et al., 2009). The observations in this experiment, therefore indicate that glyoxal was not merely partitioning into the particle phase, but was chemically transformed within or on the ammonium sulfate particles. This result is notable because the uptake and subsequent processing in the particle phase occurred at a low RH of about 31 %, where the water content of the predominantly crystalline seed aerosol particles is limited to residual or interfacial water. Highly viscous or semi-solid organic-rich particles may respond slowly to changes in gas-phase composition, particularly under dry or cold conditions (Koop et al., 2011; Mikhailov et al., 2009; Shiraiwa et al., 2013). Nevertheless, the rapid increase in the particulate organic signal after glyoxal addition suggests that reactive uptake by ammonium sulfate aerosol particles was efficient under the experimental conditions. These measurements therefore indicate that glyoxal-driven chemical aging of neutralized sulfate aerosol particles can occur even under comparatively dry and cold conditions relevant to the upper troposphere.

Before addressing further chemical processing upon irradiation, closer attention is now given to the results of the ice nucleation measurements from the aging experiment, as shown in Fig. 6.4. The top part shows the familiar trajectories of the mINKA measurements throughout the aging process. The bottom part shows four representative measurements, the times of which are indicated by triangles on the x -axis in the top part, in an AF vs. S_{ice} diagram.

Due to the background levels of ammonia mentioned before, the initial mINKA scan with the nominally pure sulfuric acid solution droplets before the deliberate addition of ammonia already featured a heterogeneous ice nucleation mode due to partial crystallization. After starting the ammonia addition, the last mINKA scan with the fully neutralized, pristine ammonium sulfate crystals (red data points in the bottom panel) showed a heterogeneous ice nucleation mode that initiated at $S_{\text{ice}} = 1.42$ and reached a maximum AF of about 1.6×10^{-3} at $S_{\text{ice}} = 1.48$. A clear change in the ice nucleation behavior was then observed after glyoxal uptake. Unlike the common suppression of heterogeneous ice nucleation activity frequently observed when organic material is added to solid ice-nucleating particles (INPs), the first mINKA scan after glyoxal injection showed a significant enhancement in ice nucleation activity (purple data points in the bottom part of Fig. 6.4). The heterogeneous ice nucleation mode shifted clearly towards a lower onset value ($S_{\text{ice}} = 1.33$) and the ice-active fractions

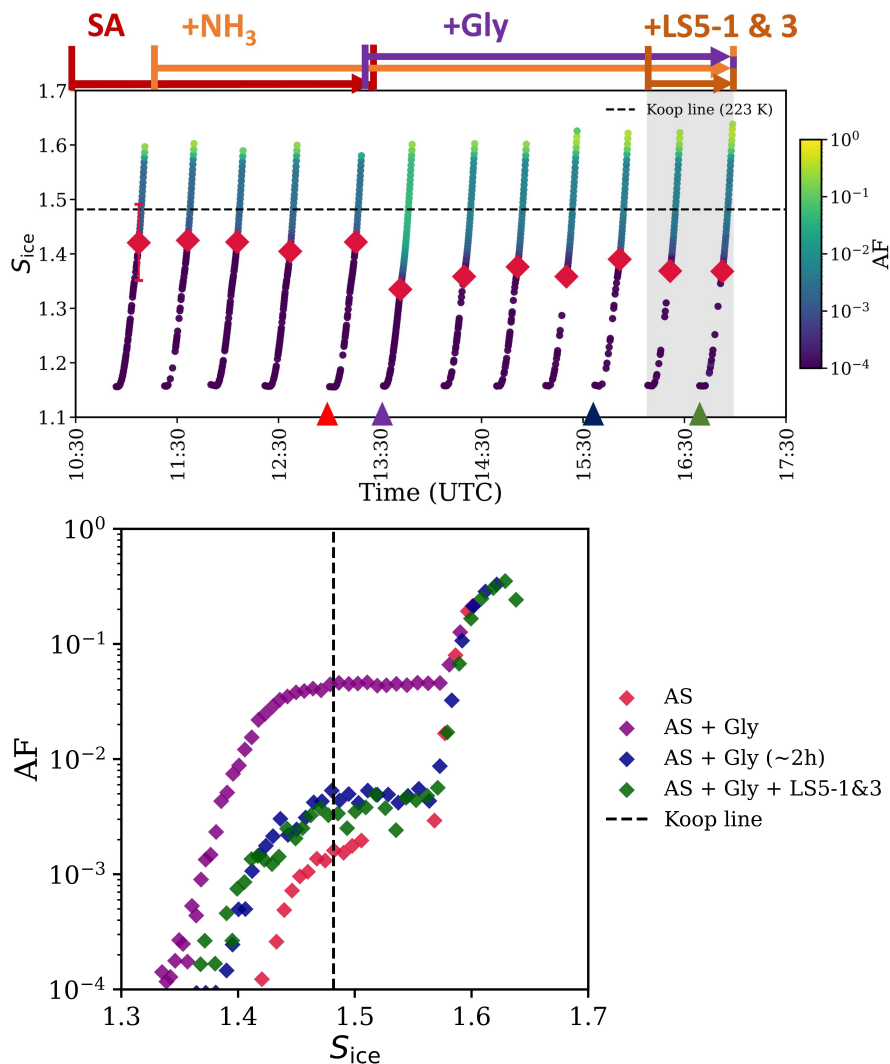


Figure 6.4: Ice nucleation measurements during the ammonium sulfate-glyoxal aging experiment. Note that the timeline starts somewhat later compared to Fig. 6.3 because a sufficient mass loading of sulfuric acid solution droplets had to be achieved before performing the first mINKA scan. Top part: trajectories of the ice nucleation measurements with mINKA throughout the aging process, using color coding to denote the ice-active fraction of the particle population. Red diamonds indicate an AF of 0.01 %. The dashed black line corresponds to the homogeneous ice nucleation threshold based on the water-activity criterion described by Koop et al. (2000). Triangles on the x -axis indicate the times of the measurements that are shown in the bottom part. Bottom part: ice nucleation activity in terms of the AF as a function of the ice saturation ratio, S_{ice} . The red data points correspond to the mINKA scan of bare ammonium sulfate (AS) particles, while the purple data points represent the first scan after glyoxal (Gly) injection under dark conditions. The blue measurement data were acquired after approximately 2 h of dark aging. The green data points show the ice nucleation ability upon continued irradiation.

increased by more than an order of magnitude, reaching values up to 4.4×10^{-2} at $S_{ice} = 1.48$. After approximately 2 h of dark aging (blue data points in the bottom part of Fig. 6.4), the heterogeneous ice nucleation activity deteriorated notably again, albeit remaining slightly higher than that of the pristine ammonium sulfate seed aerosol particles. Therefore, one might speak of a strong, “transient” increase in the heterogeneous ice nucleation ability of the seed aerosol particles, which is most evident in the early stages of chemical processing. That this transient enhancement of the ice nucleation ability is a robust and repeatable finding is evidenced by Fig. A.3, which shows the AF vs. S_{ice} plot from a second glyoxal uptake experiment on ammonium sulfate performed similarly to that shown in Fig. 6.4. However, the second glyoxal experiment was affected by cross-contamination from experiments conducted with different chemical compounds. Although a small transient enhancement is observed upon the introduction of glyoxal, further mINKA measurements resulted in lower ice onsets for chemically processed particles when compared to the bare ammonium sulfate seed aerosol particles. The further discussion focuses again on the experiment shown in Fig. 6.3, Fig. 6.4, and Fig. A.2.

Upon irradiation, photochemical processing led to a decrease in ozone, and to the production of oxidants such as OH and HO₂ radicals (Fig. A.2, panel (b)). These radicals reacted with residual gas-phase SO₂ from FLOTUS, causing an increase in the concentration of gas-phase sulfuric acid, as indicated in panel (d) of Fig. A.2. However, as shown in Fig. 6.3, this did not result in a significant change in the particle-phase composition. The effect of continued UV irradiation on the ice nucleation activity of the aerosol particle population was very small. The chemically processed and irradiated aerosol particles remained slightly more ice-active than the pristine seed particles (green data points in the bottom part of Fig. 6.4).

Additional chemical information was obtained from Filter Inlet for Gases and AEROSols (FIGAERO)-chemical ionization mass spectrometer (CIMS) filter measurements. These measurements showed the appearance of a compound with the molecular formula C₄H₅O₃N starting with the first filter sample collected after glyoxal introduction (Fig. 6.5). This formula is consistent with a nitrogen-containing product formed from glyoxal-derived chemistry, for example, through reaction of a dehydrated glyoxal dimer with ammonia or ammonium-containing particle-phase components. Ammonium ions are known to promote glyoxal reactions that form nitrogen-containing products rather than only simple hydration products or reversible oligomers (Nozière et al., 2009). The FIGAERO-CIMS measurements therefore support the conclusion that dissolved glyoxal underwent chemical transformation after uptake by the ammonium sulfate particles.

The formation of imidazole-related compounds is particularly relevant because such products are often considered relatively stable tracers of carbonyl–nitrogen chemistry and may influence aerosol optical properties (Galloway et al., 2009; Kampf et al., 2012). Previous studies

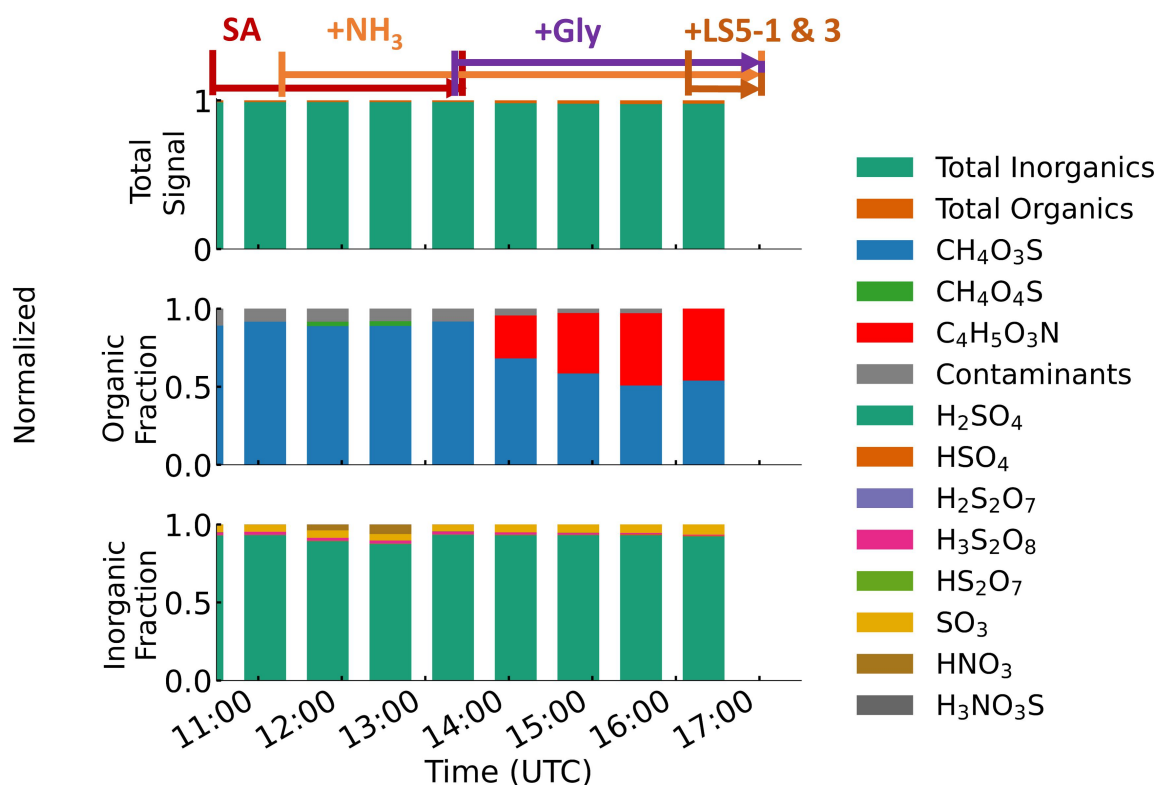


Figure 6.5: Chemical composition analysis from the FIGAERO-CIMS filter measurements during the ammonium sulfate–glyoxal aging experiment. Top panel: normalized contributions of total organics and inorganics to the aerosol chemical composition. Middle panel: fractional contribution of identified organic compounds, indicated by the respective colors, to the total organic mass of the aerosol particles. Bottom panel: fractional contribution of identified inorganic compounds, indicated by the respective colors, to the total inorganic mass of the aerosol particles.

have suggested that organosulfate formation during glyoxal uptake by ammonium sulfate aerosol particles is favored under irradiated or oxidative conditions (Galloway et al., 2009), whereas dark uptake can be at least partly reversible (Galloway et al., 2009; Kroll et al., 2005). In the present experiment, possible organosulfate formation could not be assessed directly from the available FIGAERO-CIMS measurements. Nevertheless, the observed increase in organonitrogen products suggests that ammonium-mediated carbonyl–nitrogen chemistry was an important pathway. Organosulfate formation may have occurred under irradiated conditions, but it cannot be confirmed from the present measurements. Moreover, because organosulfate formation is generally favored under highly acidic conditions (Liao et al., 2015; Surratt et al., 2010), neutralization by ammonia likely shifted the chemistry towards ammonium-mediated carbonyl–nitrogen pathways rather than organosulfate formation.

The transient nature of the ice nucleation enhancement evident in Fig. 6.4 is not yet fully understood. One possible explanation is that glyoxal uptake initially modified the surface or

near-surface structure of the ammonium sulfate particles in a way that promoted heterogeneous ice nucleation. Such modification may have involved changes in near-surface composition, surface roughness, crystallinity, or defect density, all of which could influence water adsorption and the stabilization of ice embryos. Subsequent dark aging may then have altered the chemical composition, viscosity, morphology, or surface properties of the particles, leading to a partial reduction in ice activity. Another possibility is that part of the glyoxal uptake was reversible under the relatively dry chamber conditions, as previously reported for heterogeneous glyoxal uptake on dry ammonium sulfate aerosol particles (De Haan et al., 2020). In this case, the initial enhancement may reflect an intermediate stage of chemical aging rather than a stable final particle composition.

The observed behavior is interpreted here primarily as a consequence of chemical aging rather than liquid–liquid phase separation. Glyoxal is highly oxygenated and water-soluble, so complete separation into a distinct hydrophobic organic phase is not expected. Consistent with this expectation, liquid–liquid phase separation is generally not observed in highly oxygenated organic–inorganic aerosol systems (You et al., 2013). Under the low-RH and low-temperature conditions of this experiment, glyoxal uptake by ammonium sulfate aerosol particles is therefore more plausibly described as heterogeneous reactive uptake mediated by residual or interfacial water, followed by the formation of nitrogen-containing organic products, rather than as separation into distinct organic-rich and inorganic-rich liquid phases (De Haan et al., 2020; Kampf et al., 2012; Trainic et al., 2012).

Overall, the combined chemical and ice nucleation measurements show that glyoxal uptake by ammonium sulfate aerosol particles led to measurable particle-phase chemical processing and a concurrent change in the particles' ice nucleation ability. Unlike the sulfuric acid–glyoxal and sulfuric acid–isoprene experiments, in which the particles remained largely aqueous and froze close to the homogeneous freezing threshold, the neutralized and crystalline ammonium sulfate particles were inherently heterogeneously ice-active and responded sensitively to glyoxal-driven ageing. Glyoxal uptake caused a strong transient enhancement in heterogeneous ice nucleation activity, followed by a much weaker but still elevated activity relative to the bare ammonium sulfate seed aerosol particles. These observations suggest that early-stage carbonyl–ammonium chemistry can modify the surface or bulk properties of ammonium sulfate particles in a way that temporarily promotes ice nucleation under cirrus-relevant conditions. Although the exact mechanism remains unresolved, the results demonstrate that reactive uptake of small carbonyl compounds can alter not only aerosol chemical composition, but also the ice nucleation properties of sulfate-rich particles under cold and comparatively dry upper tropospheric conditions.

6.4.2 Ice nucleation behavior of the ammonium sulfate–isoprene mixture

The previous section showed that glyoxal uptake by neutralized sulfate aerosol particles caused measurable particle-phase chemical processing and a transient enhancement in heterogeneous ice nucleation activity. To examine whether this behavior is specific to carbonyl–ammonium chemistry or represents a more general effect of organic aging, a corresponding experiment was performed with isoprene as the organic precursor. In this experiment, sulfuric acid solution droplets were again neutralized by ammonia to form crystalline ammonium sulfate seed particles, which were subsequently exposed to isoprene under dark and irradiated conditions.

The relevant gas- and particle-phase composition measurements during the ammonium sulfate-isoprene aging experiment are shown in Fig. 6.6. Chamber conditions are presented in Fig. A.4 in the appendix. Again, the neutralization by ammonia predominantly generated fully ammoniated $(\text{NH}_4)_2\text{SO}_4$ particles (dashed orange line in panel (b) of Fig. 6.6). Immediately after isoprene injection at around 21:00 UTC, only a minor increase in particle-phase organics was observed, indicating limited condensation or SOM formation under dark conditions. Upon irradiation with LS1, the reaction of OH radicals with isoprene contributed to the formation of lower-volatility oxidation products and new particles, consistent with the findings of Shen et al. (2024b). The particle formation event is visible in the size distribution measurements shown in panel (c) of Fig. A.4. The HR-ToF-AMS measurements confirm an increase in particle-phase organic material during irradiation. In parallel, the organic-to-sulfate ratio increased substantially, as shown in panel (c) of Fig. 6.6. These observations indicate that isoprene-derived SOM was formed primarily during the irradiated phase of the experiment.

The ice nucleation measurements during this experiment are shown in Fig. 6.7, with the upper part again featuring the series of mINKA humidity trajectories. Before the addition of isoprene, the bare ammonium sulfate seed particles exhibited heterogeneous ice nucleation at saturation ratios below the homogeneous freezing threshold. After isoprene was introduced under dark conditions, the ice nucleation onsets shifted slightly towards higher ice saturation ratios. This indicates a moderate suppression of the heterogeneous ice nucleation activity, even though only a small amount of particle-phase organic material was detected during the dark period. The greatest change in the ice nucleation behavior occurred after irradiation with LS1. During this period, new particle formation was observed, and the particle-phase organic fraction increased substantially. This coincided with a pronounced reduction in the heterogeneous ice nucleation activity of the seed aerosol particles. The ice nucleation onsets shifted towards the homogeneous freezing regime and occurred at saturation ratios well above those observed for the bare seed particles.

The lower panel of Fig. 6.7 illustrates this behavior in terms of the activated fraction (AF) as a function of the ice saturation ratio (S_{ice}) for three selected mINKA scans. The red data points represent the mINKA measurements of the bare ammonium sulfate seed aerosol particles.

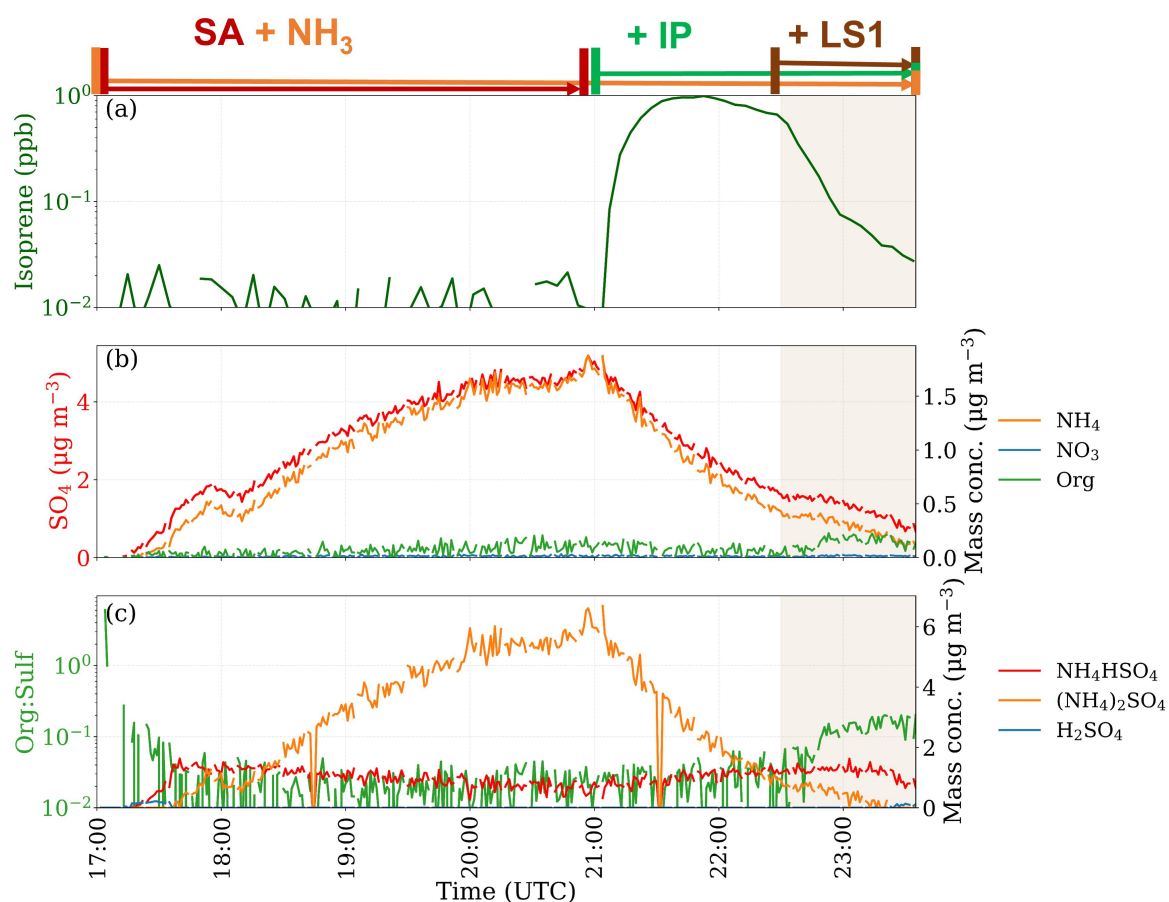


Figure 6.6: Gas- and particle-phase composition during the ammonium sulfate–isoprene aging experiment. The experimental timeline is depicted on top, with the additional shading indicating the period of irradiation with the light source LS1. In all panels, solid lines correspond to the scaling on the left axes, whereas dashed lines correspond to the right axes. panel (a): temporal evolution of the gas-phase concentration of isoprene. Panel (b): HR-ToF-AMS-derived mass concentrations of sulfate (left axis) as well as ammonium, organics, and nitrate (right axis). panel (c): organic-to-sulfate mass ratio (left axis) and estimated mass concentrations of ammonium sulfate, ammonium bisulfate, and sulfuric acid (right axis).

The green data points correspond to the aerosol population after isoprene addition under dark conditions. Compared with the bare seed particles, fewer particles nucleated ice at the same S_{ice} , confirming a moderate reduction in heterogeneous ice nucleation activity. The blue data points correspond to the mINKA scan after LS1 irradiation and represent the lowest ice nucleation activity observed during this experiment.

This behavior is consistent with the coating experiments involving dust and isoprene-derived SOM discussed in Section 4.4.3. It is also in agreement with previous studies showing that highly viscous SOM can inhibit ice-active sites on crystalline or partially crystalline seed particles and shift ice nucleation onsets to higher ice saturation ratios (Bertozzi et al.,

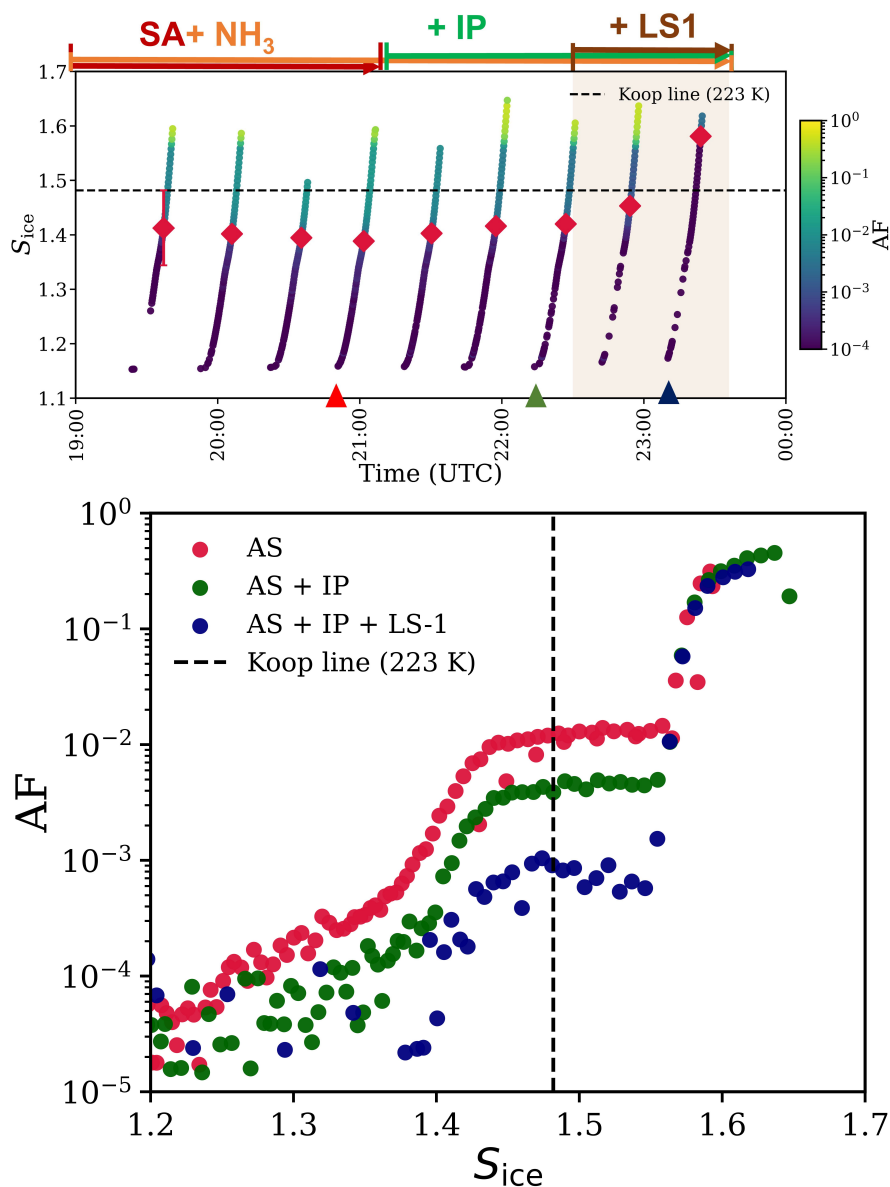


Figure 6.7: Ice nucleation measurements during the ammonium sulfate-isoprene aging experiment. Top part: trajectories of the ice nucleation measurements with mINKA throughout the aging process, using color coding to denote the ice-active fraction of the particle population. Red diamonds indicate an activated fraction of 0.1 %. The dashed black line corresponds to the homogeneous ice nucleation threshold based on the water-activity criterion described by Koop et al. (2000). Triangles on the x -axis indicate the times of the measurements that are shown in the bottom part. Bottom part: ice nucleation activity in terms of the activated fraction as a function of the ice saturation ratio, S_{ice} . The red data points correspond to the mINKA scan of bare ammonium sulfate (AS) particles, while the green data points represent the ice nucleation activity after isoprene (IP) addition under dark conditions. The blue measurement data were acquired during continued irradiation with LS1.

2021). This response contrasts with the glyoxal-aged ammonium sulfate system discussed in Section 6.4.1, where reactive uptake initially enhanced the heterogeneous ice nucleation activity. The different behavior suggests that the effect of organic aging depends strongly on the dominant chemical pathway. In the glyoxal system, carbonyl–ammonium chemistry may have temporarily modified the surface or near-surface properties of the seed particles in a way that promoted heterogeneous ice nucleation. In contrast, isoprene photooxidation appears to have mainly produced SOM that coated or passivated the ice-active ammonium sulfate surface. These results therefore indicate that organic aging of neutralized sulfate aerosol particles can either enhance or suppress heterogeneous ice nucleation, depending on the chemical nature of the organic precursor and the resulting particle-phase products.

6.5 Summary and outlook

This chapter investigated how chemically driven aging modifies the ice nucleation behavior of sulfate-containing aerosol particles. The experiments focused on the uptake and chemical processing of glyoxal and isoprene in sulfuric acid and ammonium sulfate seed aerosol particles under cold and relatively dry conditions relevant to the upper troposphere. The results show that chemical aging can either leave ice nucleation activity largely unchanged, enhance heterogeneous ice nucleation transiently, or suppress heterogeneous ice nucleation, depending on the chemical pathway and the phase state of the seed particles.

For sulfuric acid solution droplets exposed to glyoxal or isoprene, no appreciable buildup of heterogeneous ice nucleation activity was observed. Although glyoxal-related particle-phase fragments and isoprene-derived oxidized organic material were detected, the particles continued to freeze at high ice saturation ratios close to the homogeneous freezing threshold. These results suggest that the uptake or photochemical formation of organic material alone does not significantly alter the phase state of aqueous sulfuric acid solution droplets, e.g., by inducing partial crystallization or increasing the glass transition temperature to form highly viscous material. Hence, efficient heterogeneous INPs were not formed under the conditions investigated.

A different behavior was observed when sulfuric acid droplets were neutralized by ammonia to form crystalline ammonium sulfate seed particles. These particles were initially efficient heterogeneous INPs under cirrus-relevant conditions. Subsequent glyoxal uptake led to a clear increase in particle-phase organic material, nitrogen-containing fragments, and imidazole-related compounds, indicating reactive uptake and condensed-phase chemical processing. In contrast to the common suppression of heterogeneous ice nucleation by organic coatings, glyoxal aging caused a strong but transient enhancement of heterogeneous ice nucleation activity. After approximately 2 h of dark aging, the activity decreased again significantly,

but remained slightly higher than that of the bare ammonium sulfate seed particles. This suggests that early-stage carbonyl–ammonium chemistry can modify the surface or near-surface properties of ammonium sulfate particles in a way that temporarily promotes heterogeneous ice nucleation.

In contrast, the ammonium sulfate–isoprene experiment showed that isoprene-derived SOM suppressed the heterogeneous ice nucleation activity of ammonium sulfate seed particles. Under dark conditions, only a small amount of particle-phase organic material was formed and the suppression was moderate. Upon irradiation, photochemical processing produced additional low-volatility organic material and new particles, while the ice nucleation activity of the seed aerosol particles shifted towards and beyond the homogeneous freezing threshold. This behavior is consistent with the interpretation that isoprene-derived SOM coated the initially ice-active sulfate particles and reduced the accessibility of crystalline ammonium surfaces responsible for heterogeneous ice nucleation.

Taken together, the results demonstrate that the effect of organic aging on ice nucleation is not universal. Organic material does not necessarily suppress ice formation, nor does chemical aging always enhance it. Instead, the outcome depends on the chemical identity of the precursor, the neutralization state of the sulfate seed particles, the extent of particle-phase reaction, and the resulting particle morphology and phase state. Glyoxal-driven carbonyl–ammonium chemistry may temporarily increase the ice nucleation efficiency of ammonium sulfate particles, whereas isoprene-derived SOM appears to inhibit ice-active sites by coating the aerosol particle surface.

These findings have implications for ice cloud formation in the UTLS, where sulfate-containing aerosol particles are often internally mixed with organic material, ammonium, nitrate, and organosulfates. The results suggest that chemically aged sulfate-rich particles may exhibit ice nucleation behavior that differs substantially from that of pure sulfuric acid droplets, pure ammonium sulfate particles, or pure organic aerosol. Therefore, the chemical history of aerosol particles should be considered when evaluating their role in cirrus cloud formation.

Several open questions remain. First, the mechanism responsible for the transient enhancement observed after glyoxal uptake is not yet resolved. Future experiments should investigate whether this enhancement is caused by changes in near-surface composition, crystallinity, defect density, water uptake, or the formation of specific organonitrogen products. Direct measurements of particle phase state, morphology, and crystallinity would be particularly useful for constraining this mechanism. It is important to emphasize the peculiarity of observing an enhanced ice nucleation potential in comparison with that of bare ammonium sulfate crystals. All previous experiments involving compositional changes with respect to pure ammonium sulfate, including reductions in the degree of neutralization and internal

mixing with organic compounds, exhibited a consistent trend in the development of the heterogeneous ice nucleation behavior, namely a deterioration compared to pristine, fully neutralized crystals (Bertozzi et al., 2024). It was therefore suggested that parameterizations of ice nucleation based solely on ammonium sulfate (e.g., within the ice nucleation active site (INAS) approach) could lead to an overprediction of ice nucleation in cloud models if applied to the entire family of pure or internally mixed ammoniated sulfate particles (Bertozzi et al., 2024). This thesis challenges the above suggestion by revealing a pathway to improving the heterogeneous ice nucleation ability of the seed particles.

Second, the role of organosulfate formation should be examined in more detail. In the present experiments, the formation of organosulfates such as glycolic acid sulfate could not be induced through the simple introduction of sulfuric acid and glyoxal. However, previous studies indicate that enhanced acidity and the presence of NO_x can promote organosulfate formation (Surratt et al., 2008). Future experiments including NO_x would therefore allow investigation of an additional chemical aging pathway, and would help determine whether organosulfate formation modifies the phase state and ice nucleation activity of glyoxal-aged sulfate aerosol. Such experiments would also be relevant for the ATAL, where synergistic chemistry involving ammonia, glyoxal, and sulfuric acid has been linked to organosulfate-containing aerosol particles (Appel et al., 2022).

Third, future work should explore whether chemical aging can enhance ice nucleation through the formation of new crystalline or highly ordered organic–inorganic products. Biomass-burning-related secondary organic aerosol (SOA) particles formed from catechol and nitrate are a promising example, because crystalline particles have been observed as reaction products in this system (Mahrt et al., 2025). To date, however, the ice nucleation activity of such chemically aged catechol–nitrate aerosol particles has not been systematically investigated. This system could therefore provide an important test case for determining whether chemical aging can produce new ice-active aerosol particles rather than merely coating and deactivating existing ice-active surfaces.

Finally, glyoxal uptake is not limited to ammonium sulfate seed aerosol particles, but can also occur on mineral dust aerosol particles (Battaglia et al., 2025). This is relevant because mineral dust is among the most important atmospheric INP types, and chemical aging by small carbonyl compounds may modify its surface properties. This relates to the coating experiments discussed in Chapter 4 of this thesis, in which it was found that most types of coatings shielded the intrinsic heterogeneous ice nucleation ability of the feldspar particles. However, these experiments only considered the “physical” coating of the dust surface and ignored coating materials such as glyoxal, which could cause chemical aging through uptake and subsequent photochemical processing.

Overall, this chapter shows that chemically driven aging can substantially alter the ice nucleation behavior of sulfate-containing aerosol particles. The direction and magnitude of this effect depend on the interplay between inorganic seed composition, organic precursor chemistry, particle-phase reactions, and phase state. Future studies that systematically vary acidity, ammonia concentration, NO_x, oxidant level, organic loading, RH, and temperature will be essential for identifying the chemical and physical controls on ice nucleation by aged organic–sulfate aerosol particles. Such knowledge is needed to improve the representation of chemically complex aerosol particles in atmospheric models and to assess their role in cirrus formation.

7 Summary and outlook

Ice-nucleating particles (INPs) that promote heterogeneous ice nucleation in the upper troposphere – a process with significant implications for the microphysical properties of in situ formed cirrus clouds – do not always occur in their pristine form. Instead, they are frequently modified, or aged, through a range of atmospheric processes. This thesis investigated how different atmospheric aging pathways altered the ability of the particles to form cirrus clouds. The aging pathways considered were as follows: **internal mixing** – the physical conglomeration of different compositions within a single particle, specifically the condensation of secondary organic and inorganic compounds on pristine INPs; **morphological aging** resulting from particle transport and processing through deep convective clouds and/or cirrus clouds; and **chemical aging**, in which surface-level chemical reactions lead to the formation of new chemical compounds.

The research approach was founded on large-scale laboratory measurements, with the objective of realistically simulating aging pathways at low temperatures over extended time periods and through simulated cloud-processing. “Snapshots” from field measurements often reveal the complex composition of aerosol particles in the upper troposphere. By means of the controlled laboratory experiments, this thesis aimed to develop a comprehensive, process-level understanding of how these aged particles form and how their ice nucleation ability changes. Ultimately, this will provide guidance on how these aging mechanisms should be incorporated into future model studies of cirrus formation. In that sense, the laboratory measurements presented in this thesis seek to bridge the gap between field observations and modeling studies.

More specifically, the Aerosol Interaction and Dynamics in the Atmosphere (AIDA) cloud chamber at Karlsruhe Institute of Technology (KIT) and the Cosmics Leaving Outdoor Droplets (CLOUD) facility at European Organization for Nuclear Research (CERN) were used as low-temperature “reaction tanks” to simulate the various aging mechanisms, while the evolution of the ice nucleation ability of the aerosol particles was continuously measured using two Continuous Flow Diffusion Chambers (CFDCs): mobile Ice Nucleation instrument of the Karlsruhe Institute of Technology (mINKA) and Ice Nucleation instrument of the Karlsruhe Institute of Technology (INKA). The particular experimental benefits of the AIDA chamber included the ability to conduct aging experiments over many hours to gradually increase the thickness of the coating of secondary organic and inorganic compounds on pristine INPs; the ability to perform a “super-expansion” with an additional expansion volume

to subject the entire aerosol population to ice cloud-processing; and the ability to sample temperature-labile particle morphologies with an unbroken cold chain for Environmental Scanning Electron Microscope (ESEM) measurements. At CLOUD, the newly developed aerosol generator, FLOW Tube System (FLOTUS), and the comprehensive suite of gas and particle mass spectrometers were helpful in providing a detailed characterization of the chemical modifications undergone by the aerosol particles.

Internal mixing of mineral dust particles. Mineral dust particles are recognized as an important INP type under cirrus conditions, and parameterizations based on the ice nucleation active site (INAS) approach exist to describe the ice nucleation activity of bare, pristine particles in cloud models (Ullrich et al., 2017). The first set of aging experiments presented in this thesis demonstrated that many organic and inorganic coating materials effectively impeded, or “blocked,” the intrinsic heterogeneous ice nucleation ability of K-feldspar particles – the employed proxy for mineral dust – under cirrus conditions (223 K). This suggests that introducing the class of “coated dust” in cloud models is indispensable to account for their reduced ice nucleation ability in an internal mixing state. A limitation of these coating experiments conducted in the AIDA chamber was that the coating thickness could not be exactly determined; however, it was so small that it did not notably change the size of the dust mode in the size distribution measurements. Coatings of aqueous sulfuric and nitric acid shifted the ice nucleation onset of the K-feldspar particles to the homogeneous freezing threshold. An ice nucleation onset even slightly beyond this threshold was observed in the case of a coating with viscous organic material from the oxidation of isoprene, presumably due to delayed liquefaction. These findings agree with a handful of previous AIDA experiments using K-feldspar coated with sulfuric acid and secondary organic material (SOM) from α -pinene ozonolysis (Bertozzi et al., 2021).

A new aspect of this thesis was the neutralization of acidic coating layers by ammonia. This increases the complexity of the system because, once ammoniated, either sulfuric acid or nitric acid might effloresce heterogeneously on the surface of the K-feldspar particles, yielding crystalline ammonium sulfate or ammonium nitrate. Unlike ammonium nitrate, the ammonium sulfate coating may, in principle, also crystallize homogeneously. However, the coating experiments were conducted at ambient conditions above its homogeneous efflorescence relative humidity. As crystalline ammonium sulfate or ammonium nitrate are both well-recognized INP types under cirrus conditions, the coated dust particles may exhibit heterogeneous ice nucleation again after neutralization. However, this is now due to the crystalline coating layer. Experimentally, the “reappearance” of heterogeneous ice nucleation was only observed in the case of the K-feldspar – ammonium nitrate system. This phenomenon was absent in the respective experiment involving K-feldspar and ammonium sulfate. It was also not detected in a single test experiment under the same temperature and humidity conditions

involving field-collected Asian dust particles coated with nitric acid and then neutralized with ammonia. This finding suggests that the efficiency of heterogeneous efflorescence is dependent on both the nature of the dust core and the inorganic solute, and may be governed by the crystal match between the dust surface and the inorganic crystal. A set of additional measurements using various types of mineral dust particles with different mineralogical compositions is required in order to determine whether the heterogeneous efflorescence of ammonium nitrate-coated particles is a widespread phenomenon. The atmospheric significance of this process lies in its potential to contrast the prevalent passivation of the ice nucleation potential of dust particles by aqueous or viscous coating layers. Consequently, the particle class of "coated dust" in cloud models may still preserve a certain degree of heterogeneous ice nucleation ability.

Morphological aging of secondary organic aerosol (SOA) particles. Under the temperature and humidity conditions of the upper troposphere, SOA particles are predominantly in an amorphous solid, glassy state. Although they principally offer a solid surface on which heterogeneous ice nucleation can occur, pure SOA particles or dust particles coated with SOM (see the K-feldspar–isoprene experiment mentioned above) are generally observed to nucleate ice only at or above homogeneous freezing conditions. This ultimately led to the recommendation that they should be treated as ice-inactive in models (Kasparoglu et al., 2022). The experiments conducted in this thesis demonstrate that this recommendation also applies to pure SOA particles that have undergone morphological aging through ice-cloud processing, resulting in porous or irregular surface features, as opposed to the smooth surface of pristine particles. This morphology change is due to the re-vitrification of temporarily liquefied organic material on the nucleated ice crystals. After sublimation, open network or pore structures are left behind where the ice once was (Adler et al., 2013). Morphological changes are more pronounced in deep-convective cloud processing, where the entire SOA particles temporarily liquefy, than in cirrus cloud processing, where only the outer layers of the particles liquefy. However, as was observed in this thesis with isoprene-derived SOA particles, both types of ice cloud-processing simulated in the AIDA chamber only marginally reduced the ice nucleation onsets compared with the pristine, compact particles. This finding supports earlier AIDA experiments that used a different precursor for SOA formation, namely α -pinene (Wagner et al., 2017; Wagner et al., 2024). The slight increase in the ice nucleation ability of the SOA particles following ice cloud-processing may be due to an increased surface area, or a “memory” effect whereby the ice crystals leave an “imprint” on the glassy material, pre-activating the particles. However, even subsequent to ice cloud-processing, the ice nucleation onsets of the SOA particles remained in proximity to the conditions under which ubiquitous aqueous solution droplets would freeze homogeneously, thus rendering them an irrelevant INP type.

The situation may change completely when not considering pure SOA particles, but SOM-coated dust particles. Earlier AIDA experiments involving α -pinene-derived SOM showed that an initially uniform SOM coating layer on dust particles may be detached from the dust surface through deep-convective cloud processing, re-exposing active sites for heterogeneous ice nucleation (Wagner et al., 2024). Unfortunately, due to the decommissioning of the AIDA chamber, it was not possible to repeat such experiments and confirm their outcomes within the time frame of this thesis using SOM from isoprene oxidation. This remains an important topic for future chamber experiments. It also highlights the intricate nature of different aging pathways and the fact that it is often not possible to discuss one pathway without considering the others: **internal mixing** by SOM coating might lead to a complete passivation of the dust particle surface in terms of heterogeneous ice nucleation, but **morphological aging** through ice cloud-processing might re-activate the ice nucleation potential of the particles.

Chemical aging of sulfate-containing seed aerosol particles. The reactive uptake of organic precursors is an important process by which sulfate-containing seed particles can acquire the chemical complexity observed in particles in the upper troposphere, for example, in the Asian Tropopause Aerosol Layer (ATAL) layer. In dedicated chemical aging experiments conducted at the CLOUD chamber facility at CERN, two types of seed aerosol particles (aqueous sulfuric acid solution droplets and crystalline ammonium sulfate particles) were exposed to two types of organic precursors: glyoxal and isoprene. First, the uptake was investigated in the dark, without illumination. Later, it was investigated during photochemically active conditions, with the production of OH radicals through UV photolysis of ozone. Although glyoxal is an important precursor whose uptake chemistry at warmer temperatures and different relative humidity (RH) conditions has been widely studied, this thesis is among the first to investigate the ice nucleation activity of “glyoxal-aged” particles under cirrus-relevant conditions.

Exposure of acidic sulfuric acid solution droplets to either glyoxal or isoprene resulted in the detection of glyoxal-related particle-phase fragments or isoprene-derived oxidized organic material by mass spectrometry. However, it appears evident that no crystalline or highly viscous particle components were formed, as the seed particles continued to nucleate ice at the homogeneous freezing threshold. In the case of crystalline ammonium sulfate, the time series of CFDC measurements during aging started with a heterogeneous nucleation mode for the pristine seed particles. Processing with isoprene-derived SOM produced a similar result to that seen in the internal mixing experiments with the K-feldspar particles. The viscous SOM material that condensed on the inorganic crystals shielded their intrinsic heterogeneous ice nucleation ability. The result observed for glyoxal uptake was completely different and surprising. Following the start of glyoxal addition, the first CFDC humidity scan revealed that the efficiency of the heterogeneous ice nucleation mode of the seed aerosol particles,

as measured by the ice-active fraction, had increased by over an order of magnitude. This increase was transient in nature, as subsequent CFDC measurements revealed a reduction in the activated fractions under dark and later irradiation conditions. However, the ice-active fractions remained slightly above those of the pure ammonium sulfate seed particles.

Mass spectrometry measurements revealed the formation of organonitrogen and imidazole-related compounds following the addition of glyoxal. However, the exact mechanism giving rise to the transient increase in heterogeneous ice nucleation activity remains uncertain. The observed phenomenon may be associated with alterations in the surface or near-surface properties of the crystals during early-stage carbonyl–ammonium chemistry. This finding adds to the complexity of determining how ammonium sulfate crystals should be treated in models of cirrus formation. Until now, a couple of processes have been identified that could reduce the ice nucleation activity compared with pure, fully neutralized ammonium sulfate particles, including, e.g., partial neutralization and internal mixing with organic matter. Therefore, it was suggested that using a parameterization based on the inferred INAS densities of pure ammonium sulfate might lead to ice formation being overpredicted in cirrus cloud models (Bertozzi et al., 2024). Here, however, a process was identified that could even increase the seed particles' ice nucleation potential.

Concluding remarks. This thesis clearly illustrates the potential of large cloud chamber facilities to realistically simulate a variety of significant atmospheric aging pathways. From the laboratory perspective, the work has demonstrated what can be achieved experimentally in terms of addressing the effect of aging on ice nucleation for relevant particle classes. It is expected that the successor to the dismantled “classic” AIDA vessel, the Aerosol Interaction and Dynamics in the Atmosphere cold and clean (AIDAc2) chamber, will also be well-suited to pursuing this topic on an experimental basis. In fact, the planned extension of the chamber to include a powerful UV illumination system and single-particle mass spectrometry measurements as a standard instrumentation tool, as well as the expected cleaner vacuum conditions resulting from full-metal sealings, may improve the chamber's capability to perform dedicated chemical aging experiments, which can currently only be conducted at the CLOUD facility. This paves the way for further laboratory studies to systematically investigate how coating thickness, oxidation state, viscosity, neutralization degree, crystallinity, and particle morphology influence ice nucleation across a wider range of atmospheric particle classes.

Apart from the experimental aspect, the summary has already alluded to the enormous challenges involved in adequately considering all these aging processes in cloud models. Future cloud chamber experiments should therefore be conducted in close collaboration with the modeling community, with the ultimate goal of deriving a more realistic parametrization for the ice nucleation activity of aged aerosol particles in cloud models. Such models may also be validated in the future by in situ field measurements. PINEair, the airborne extension

of the Portable Ice Nucleation Experiment (PINE) family, offers a promising new method for measuring the real-time ice nucleation efficiency of upper-tropospheric aerosol particles during flight campaigns. Combining PINEair, cloud probes, and onboard aerosol mass spectrometers in future aircraft campaigns will be particularly valuable for linking the chemical composition of aerosol particles directly to their ice nucleation activity under upper-tropospheric conditions.

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Abbreviations

AF	activated fraction
AIDA	Aerosol Interaction and Dynamics in the Atmosphere
AIDAc2	Aerosol Interaction and Dynamics in the Atmosphere cold and clean
APC	Aerosol Preparation and Characterization
APicT	AIDA PCI in-cloud Tunable diode laser
APS	Aerodynamic Particle Sizer
ATAL	Asian Tropopause Aerosol Layer
CCN	cloud condensation nuclei
CERN	European Organization for Nuclear Research
CFDC	Continuous Flow Diffusion Chamber
CIMS	chemical ionization mass spectrometer
CLOUD	Cosmics Leaving Outdoor Droplets
CNT	Classical Nucleation Theory
CPC	Condensation Particle Counter
DMA	differential mobility analyzer
DRH	deliquescence relative humidity
ESEM	Environmental Scanning Electron Microscope
FDRH	full deliquescence relative humidity
FIGAERO	Filter Inlet for Gases and AEROsols
FLOTUS	FLOw TUBE System
GCR	Galactic Cosmic Ray
GV	gate valve
HR-ToF-AMS	high-resolution time-of-flight Aerosol Mass Spectrome- ter
INAS	ice nucleation active site

INKA	Ice Nucleation instrument of the Karlsruhe Institute of Technology
INP	ice-nucleating particle
KIT	Karlsruhe Institute of Technology
LDI	Laser Desorption and Ionization
LS	light sabre
lSMPS	long SMPS
MD	Molecular Dynamics
mINKA	mobile Ice Nucleation instrument of the Karlsruhe Institute of Technology
nSMPS	nano SMPS
PALMS-NG	Particle Analysis by Laser Mass Spectrometry-Next Generation
PCF	pore condensation and freezing
PINE	Portable Ice Nucleation Experiment
PS	Proton Synchrotron
PTFE	polytetrafluoroethylene
QC-TILDAS	Quantum Cascade Tunable Infrared Laser Differential Absorption Spectrometer
RH	relative humidity
SIMONE	Streulichtintensitätsmessungen zum optischen Nachweis von Eispartikeln
SMPS	Scanning Mobility Particle Sizer
SOA	secondary organic aerosol
SOM	secondary organic material
TDL	Tunable Diode Laser
TME	tetramethylethylene
UTLS	Upper Troposphere Lower Stratosphere
VOC	volatile organic compound

Appendix

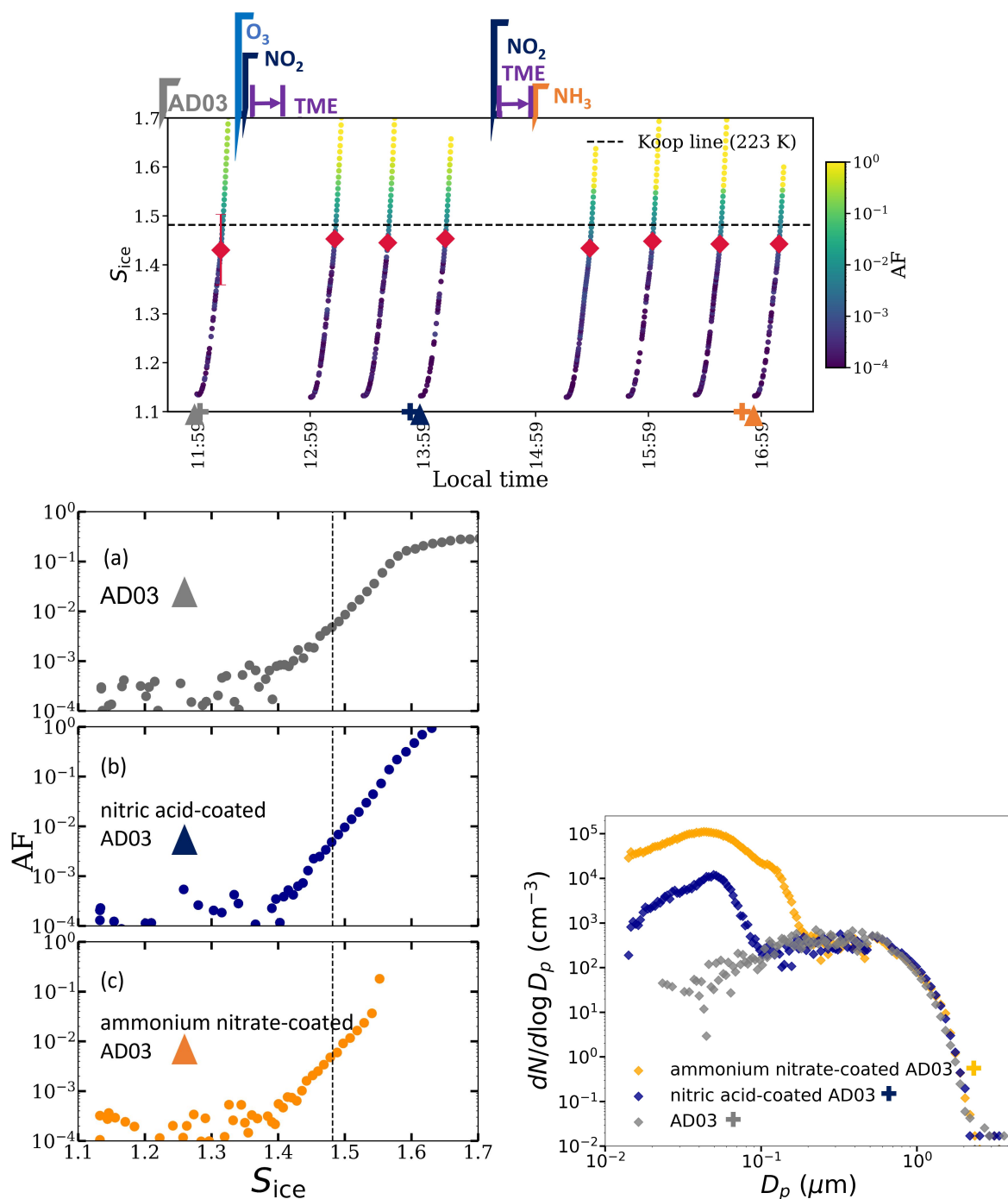


Figure A.1: Overview of the coating experiment where the aqueous nitric acid-coating over AD03 particles was neutralized by ammonia. Top part: Trajectories of the ice nucleation measurements with mINKA throughout the coating process, using color coding to denote the ice-active fraction of the sampled aerosol particles. Colored triangles and plus signs on the time axis indicate when the mINKA scans and size distribution measurements, shown in the bottom-left and bottom-right parts, respectively, were performed. The addition of trace gases is symbolized at the top. Red diamonds indicate an activated fraction of 0.1%. *Caption continued on next page.*

Caption continued. Bottom left: ice-active fractions as a function of ice saturation ratio from mINKA scans with the bare AD03 particles (panel (a), gray), nitric acid-coated AD03 particles (panel (b), blue), and ammonium nitrate-coated particles after NH_3 injection (panel (c), orange). Bottom right: combined SMPS-APS size distribution measurements of the bare (gray), nitric acid-coated (blue), and ammonium nitrate-coated (orange) dust particles. As shown by the labels at the top, the experiment involved the following steps: ozone was just added once at the start of the coating process at 12:20:00 local time (982 ppb). The successive coating steps then involved the pairwise addition of NO_2 and tetramethylethylene (TME) starting at 12:23:00 (104 ppb NO_2 and 5.95 ppb min^{-1} TME for 17 min) and at 14:30:00 (104 ppb NO_2 and 5.95 ppb min^{-1} TME for 23 min), followed by the introduction of ammonia (175 ppb) at 15:00:00 local time.

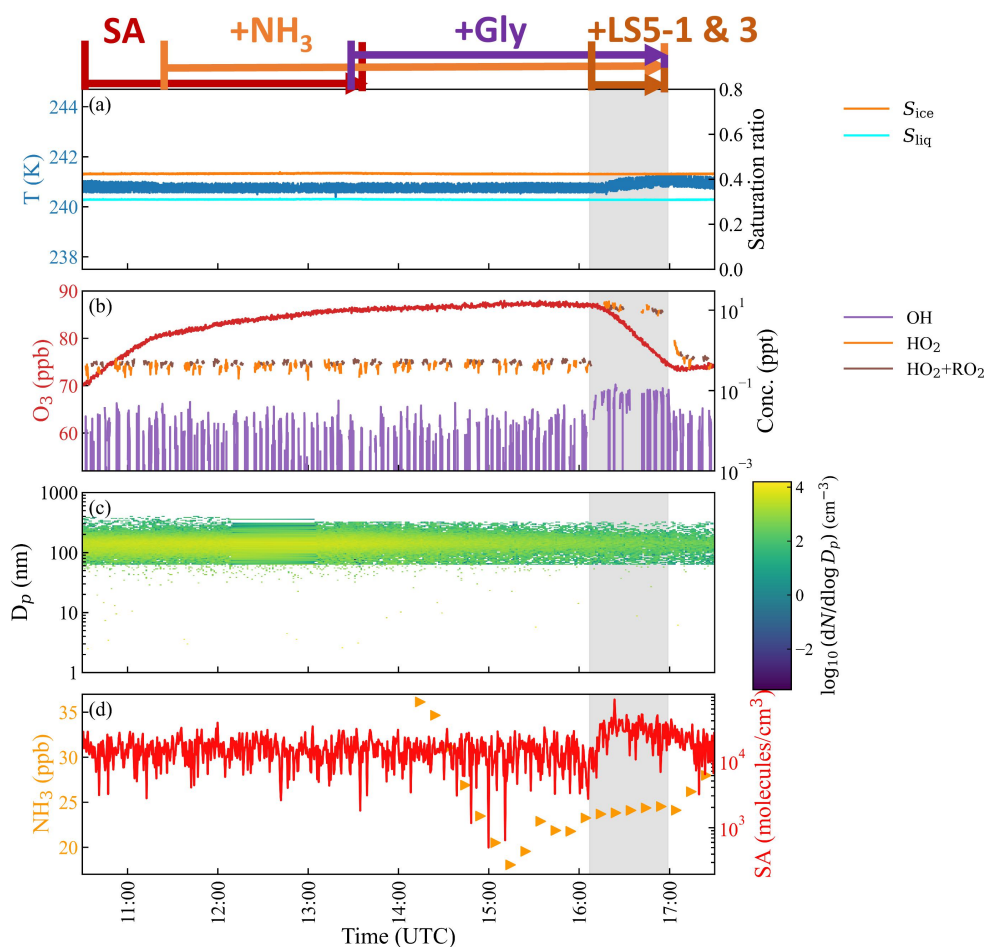


Figure A.2: Chamber conditions during the ammonium sulfate-glyoxal aging experiment. Panel (a): chamber gas temperature (T , left axis) and saturation ratios with respect to supercooled water and ice (right axis). Panel (b): ozone concentration (left axis) and O_3 -derived radicals during irradiation (right axis). Panel (c): combined size distribution measurements from the nSMPS and lSMPS instruments. Panel (d): gas-phase concentrations of ammonia (NH_3) (left axis, data available only after 14:00:00 UTC due to instrumental problems) and sulfuric acid (SA) (right axis). The shading indicates the period of irradiation with LS5 lamps 1 and 3.

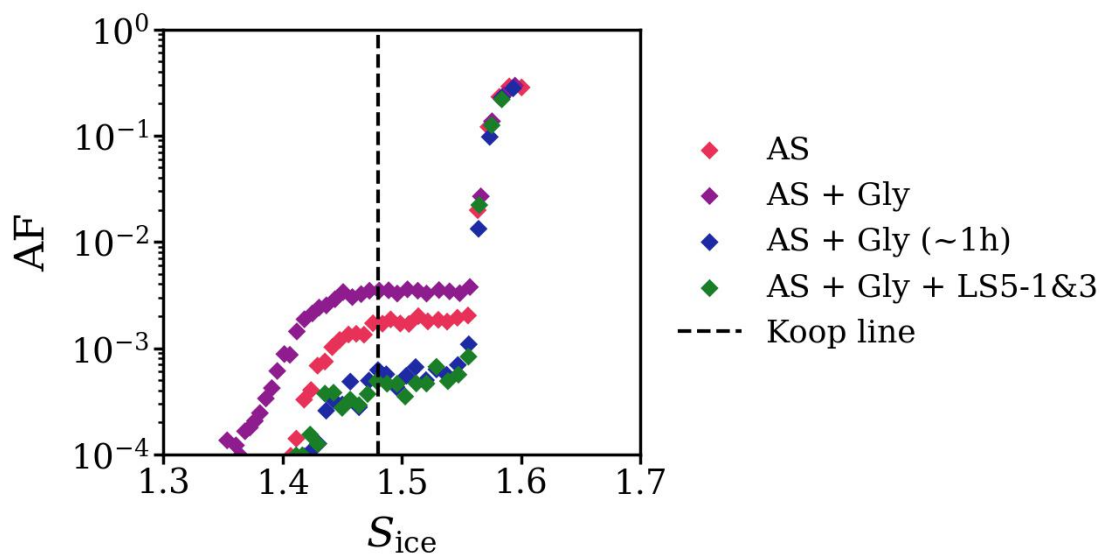


Figure A.3: Second glyoxal uptake experiment on crystalline ammonium sulfate seed particles, the measurement data of which may be biased by cross-contamination from other CLOUD experiments. Ice nucleation activity in terms of the activated fraction (AF) as a function of the ice saturation ratio, S_{ice} . The black dashed line indicates the homogeneous freezing threshold at 223 K according to Koop et al. (2000). The red data points correspond to the mINKA scan of bare ammonium sulfate (AS) particles, while the purple data points represent the first scan after glyoxal (Gly) injection under dark conditions. The blue measurement data were acquired after approximately 1 h of dark aging. The green data points show the ice nucleation ability upon continued irradiation.

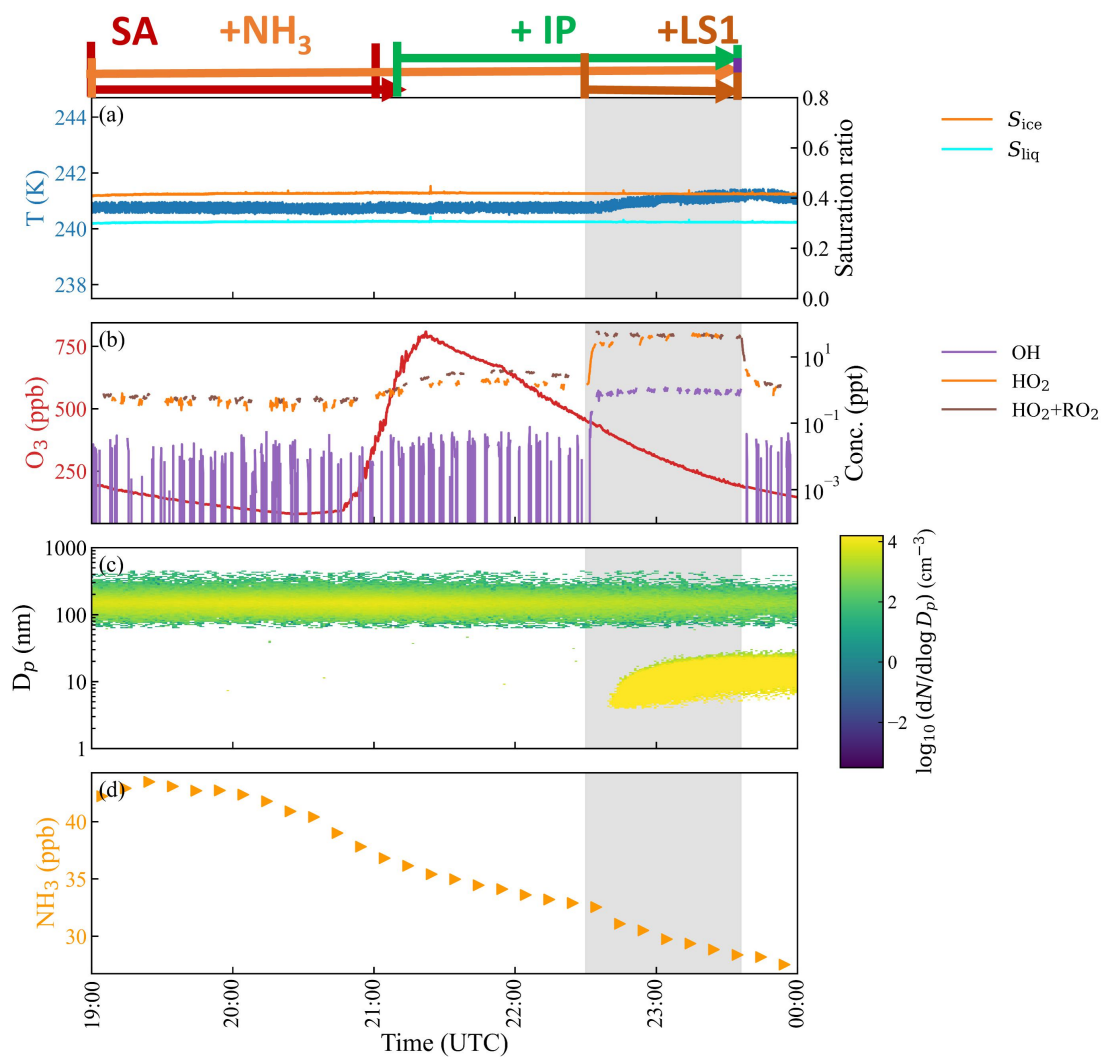


Figure A.4: Chamber conditions during the ammonium sulfate-isoprene aging experiment. Panel (a): chamber gas temperature (T , left axis) and saturation ratios with respect to supercooled water and ice (right axis). Panel (b): ozone concentration (left axis) and O_3 -derived radicals during irradiation (right axis). Panel (c): combined size distribution measurements from the nSMPS and ISMPS instruments. Panel (d): gas-phase concentrations of ammonia (NH_3). The shading indicates the period of irradiation with the light source LS1.

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