Chapter 8

Measurements of Ice Nucleating Particles and Ice Residuals

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ABSTRACT

It has been known that aerosol particles act as nuclei for ice formation for over a century and a half (see Dufour). Initial attempts to understand the nature of these ice nucleating particles were optical and electron microscope inspection of inclusions at the center of a crystal (see Isono; Kumai). Only within the last few decades has instrumentation to extract ice crystals from clouds and analyze the residual material after sublimation of condensed-phase water been available (see Cziczo and Froyd). Techniques to ascertain the ice nucleating potential of atmospheric aerosols have only been in place for a similar amount of time (see DeMott et al.). In this chapter the history of measurements of ice nucleating particles, both in the field and complementary studies in the laboratory, are reviewed. Remaining uncertainties and artifacts associated with measurements are described and suggestions for future areas of improvement are made.

1. A history of ice nucleating particle measurements

a. The difference between ice nucleating particles and ice residuals

The idea that small particles that originate from Earth's surface initiate ice formation in the atmosphere was suggested by Dufour (1862), who found that hailstones contained small sand, ash, or chaff. It is now understood that these inclusions often initiate nucleation of the ice phase either via deposition of water vapor to their surface or from within a supercooled liquid water droplet; they are termed ice nucleating particles (INPs; all acronyms additionally defined in Table 8-1) (Vali et al. 2015). After ice formation, riming, scavenging, and aggregation may lead to the collection of additional particles by a growing ice crystal and

chemical reactions may take place on the ice crystals' surface. Dissolution of the original INP and ice multiplication processes can form ice particles that do not contain an INP. Particles remaining after evaporation of ice in hydrometeors are called ice residuals (IRs). To date, attempts to compare ice number density to residuals have proven difficult because of shattering of ice crystals on cloud probes (Korolev and Isaac 2005; Cziczo and Froyd 2014). For these reasons, IRs and INPs cannot currently be assumed to be identical.

Nevertheless, atmospheric IRs have been studied to understand which particles initiated the formation of ice crystals. One technique is to examine particles located at the crystallographic center of ice crystals by means of microscopy (Rogers and Vali 1978). Newly formed ice crystals likely contain only the INP as they have not been

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TABLE 8-1. List of acronyms.

Expansion	Acronym
Aerosol interaction and dynamics in the atmosphere	AIDA
Attenuated total reflectance FTIR	ATR-FTIR
Bielefeld ice nucleation array	BINARY
Black carbon	BC
Cloud condensation nuclei	CCN
Continuous flow diffusion chamber	CFDC
Colorado State University–immersion mode ice spectrometer	CSU-IS
Contact ice nucleation chamber	CINC
Cloud and Aerosol Characterization Experiment	CLACE
Collision ice nucleation chamber	CLINCH
Cold stage	CS
Counterflow virtual impactor	CVI
Droplet evaporation unit	DEU
Drop freezing arrays	DFA
Differential scanning calorimeter	DSC
Electrodynamic balance	EDB
Energy-dispersive X-ray spectroscopy	EDX
Electron microscopy	EM
Environmental SEM	ESEM
Field emission gun	FEG-SEM
Fast Fourier transformation	FFT
Fast ice nucleation chamber	FINCH
Frankfurt Ice Deposition Freezing Experiment	FRIDGE
Fourier transform infrared spectroscopy	FTIR
Immersion mode cooling chamber	IMCA
Ice nucleation active site densities	INAS
Ice nucleating particles	INP
Ice residuals	IR
Ice selective inlet	ISI
Leipzig aerosol cloud interaction simulator	LACIS
Limit of detection	LOD
Manchester ice cloud chamber	MICC
Massachusetts Institute of Technology–collision efficiency chamber	MIT-CEC
Mixed-phase cloud	MPC
Microlitre nucleation by immersed particle instrument	μl-NIPI
Near-edge absorption fine structure spectroscopy	NEXAFS
North Carolina	NC
Optical trap	OT
Pumped counterflow virtual impactor	PCVI
Portable immersion mode cooling chamber	PIMCA
Portable ice nucleation chamber	PINC
Scanning EM	SEM
Spectrometer ice nuclei	SPIN
Single-particle mass spectrometer	SPMS
Scanning transmission X-ray microscopy	STXM
Transmission (or tunneling) EM	TEM
Temperature gradient diffusion chamber	TGDC
Time of flight	ToF
Ultraviolet	UV
Vacuum chamber	VC
Wind tunnel	WT
X-ray diffraction	XRD
Zurich ice nucleation chamber	ZINC

exposed to extensive processing. They have been sampled using counterflow virtual impactors (CVIs) from aircraft to study cirrus IRs (e.g., Ogren et al. 1985; Noone et al. 1988; Twohy et al. 1997; Cziczo et al. 2004) or in special ground-based inlets to study IRs from mixed-phase clouds (MPCs) (Mertes et al. 2007; Kupiszewski et al. 2015).

Sampling INPs follows a different approach whereby particles, either airborne or on a substrate, are exposed to known thermodynamic conditions and the occurrence of ice formation is monitored. Various techniques have been developed since the first half of the twentieth century to study the different ice formation mechanisms (Kanji et al. 2017, chapter 1). An overview of the most important techniques and results is also given here.

b. Ground-based studies

For ground-based examinations there are three main approaches: investigating collected precipitation (IRs), studying the formation of ice on ambient particles (INPs), and examining MPCs directly (IRs).

1) MEASUREMENTS OF INPs AND IRs IN COLLECTED PRECIPITATION

Isono (1955) in Japan and Kumai (1961) in the United States analyzed the particles found in collected ice crystals by means of electron microscopy (EM) and both found clay minerals to be the main IRs. Although mineral material is still considered the dominant INP type by number, in the following years biological IRs were also detected (Szyrmer and Zawadzki 1997 and references therein). The use of drop freezing arrays (DFA) by Bigg (1953) was an early technique that allowed determination of freezing onset temperature and frozen fractions. Vali (1966) estimated atmospheric INP concentrations, by the definition here assuming INP number concentration was equivalent to that measured for IRs, based on volume of melted hail and rainwater from initial ice-phase precipitation.

2) AMBIENT AEROSOL PARTICLES AS INPs

To determine the INP concentration, two methods have been used: online (such as cloud or continuous flow chambers) and offline (where particles are collected on a substrate and subsequently exposed to controlled conditions).

INPs were initially studied in the laboratory starting as early as the mid-1940s, when Vonnegut (1947), motivated by cloud seeding, not atmospheric INPs, sought to identify and characterize the activity of potent INPs. Vonnegut used an early cloud chamber to show that a man-made INP, silver iodide, nucleated ice between $-4°$ and $-8°C$. The main mechanisms for chambers being used at that time were either expansion (i.e., lowering the pressure) or on injection of hot steam in a cooled chamber (i.e.,
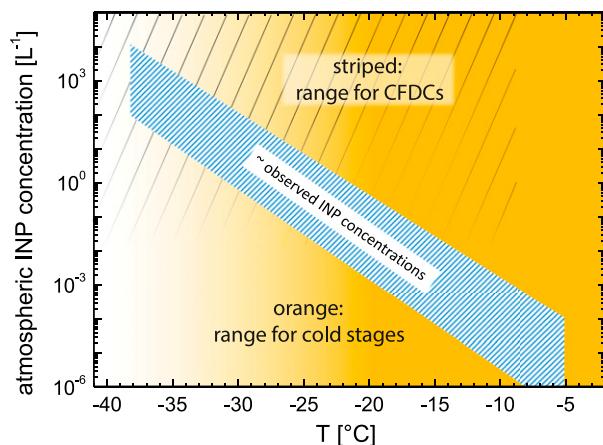
FIG. 8-1. The range of INP concentration observed for ambient aerosols vs temperature. The common temperature ranges of CFDC (Table 8-2) and cold-stage (Table 8-3) instruments are given for context (DeMott et al. 2011 and references therein).

supersaturation). Online methods were also developed as early as the 1940s for in situ aircraft measurements of INPs (e.g., Palmer 1949; Langer et al. 1967). With secondary ice formation and crystal shatter artifacts not yet known, INP and ice crystal concentrations were often assumed to be identical. This changed when Mossop (1970) and Hallett and Mossop (1974) first suggested secondary ice production mechanisms in clouds and when Korolev and Isaac (2005) quantified ice shattering on cloud probes.

Today, the most common in situ and laboratory chambers are variants of the continuous flow diffusion chamber (CFDC; Rogers 1988), which uses supersaturation derived from two ice-coated plates held at different temperatures (section 2a). Several larger, nonportable systems are currently in use for laboratory studies of specific materials. They are based on the expansion principle (e.g., Möhler et al. 2003; Connolly et al. 2012), on heat-vapor diffusion (Hartmann et al. 2011), or mixing of cold and dry air with warm and humidified air (Bundke et al. 2008) (see Kanji et al. 2017, chapter 1, and section 2).

Offline methods for INP determination were initially derived from aerosol filter collections. Subsequent analysis is performed by exposing the filter to controlled supersaturation and temperature and observing ice formation. This is either done in deposition/condensation mode by controlling the temperature and humidity above the filter or for aerosol immersed in water droplets prior to cooling (e.g., Schnell 1977; Rosinski et al. 1986).

DeMott et al. (2015) found good agreement when comparing INP concentrations derived by online and offline methods. As a whole, measurements have demonstrated an exponential increase in INP concentration with decreasing temperatures (Fig. 8-1; see additional description in Kanji et al. 2017, chapter 1). With

variability up to seven orders of magnitude (DeMott et al. 2010, 2016; Petters and Wright 2015), it remains to be determined what fraction of this is due to natural versus instrumental differences (DeMott et al. 2011).

Historically, laboratory measurements were sometimes motivated by determination of ice activity of various samples without considerable connection to their atmospheric abundance. Foremost among these were man-made substances such as silver iodide that were studied for their use in weather modification (Vonnegut 1947). Natural samples such as soil dusts, leaf litter, seawater, and bacterial samples were also studied, often motivated by collections of fog water and precipitation (e.g., Schnell and Vali 1976; Vali et al. 1976; Schnell 1977).

3) IRs IN MIXED-PHASE CLOUDS

There exist two ground-based CVI inlet systems for sampling IRs of ice crystals contained in MPCs. These are the Ice-CVI (Mertes et al. 2007) and Ice Selective Inlet (ISI; Kupiszewski et al. 2015), both of which have been deployed at the high-altitude research station Jungfraujoch in the Swiss Alps (3580 m MSL; section 2b).

The Ice-CVI was operated during the Cloud and Aerosol Characterization Experiment (CLACE) for which Mertes et al. (2007) presented an ice activated fraction as a function of particle size. Assuming the IRs to be the original INPs, they concluded that the particles' efficiency to nucleate ice increases with size. A higher concentration of IRs with diameters below 1 μm was found than those in the supermicrometer range. A higher abundance of submicrometer-diameter IRs was also found by Kupiszewski et al. (2016) although these findings are not in agreement with the finding of larger, often supermicrometer, particles by Cziczo et al. (2013) and Mason et al. (2016).

Several studies have been carried out to determine IR chemical composition. It should be noted that these are location-specific findings and, because of the limited number of measurements to date, these should not yet be taken as general findings. An enrichment of black carbon (BC) mass in IRs was observed using a filter-based light transmission method (CLACE 3; Cozic et al. 2008; Mertes et al. 2007) and using EM (CLACE 5; Ebert et al. 2011). Although the signals from ice nucleation and scavenging were not directly differentiated, the size limit of the ice crystals sampled ($<20\,\mu$m diameter) was noted to allow minimal scavenging time after nucleation. In contrast, no enrichment of BC in IRs was found for CLACE 6 (Kamphus et al. 2010) and CLACE 2013 (Kupiszewski et al. 2016; Worringen et al. 2015) using single-particle mass spectrometry, laser-induced incandescence measurements, and EM. Another chemical fingerprint in the Ice-CVI measurements was the detection of lead in the IRs, which was substantially enhanced, compared to the

background aerosol population (Cziczo et al. 2009; Ebert et al. 2011; Worringen et al. 2015) and is known to be an efficient INP type (Cziczo et al. 2009). In general, the aforementioned studies identified mineral dust (silicates) as the dominant IR, and presumably INP, component. The existence of biological particles in the IRs was investigated by Kupiszewski et al. (2015) who found an enrichment of fluorescent particles compared to the background aerosol during a Saharan dust event in the sub-2-μm IRs.

c. Aircraft-based studies

The first airborne efforts to understand the nature of ice nucleation in clouds was performed in the early 1990s using a CVI to separate ice crystals from other particles (Noone et al. 1992; Ström and Heintzenberg 1994; Heintzenberg et al. 1996; Ström et al. 1997; Seifert et al. 2003, 2004). These initial studies sublimated condensed-phase water and performed counts, and later sizing, of the residual particles. As described in section 3b, it is highly likely that these initial efforts were subject to undetected artifacts associated with ice impaction on aircraft and inlet surfaces.

Later studies collected particles for offline analysis, for example, by EM (Petzold et al. 1998; Twohy and Gandrud 1998; Twohy and Poellot 2005; Targino et al. 2006; Cziczo et al. 2013), and these are more fully described in section 2c. Since the early 2000s, the most common technique is the online, real-time mass spectrometer described in section 2d. (Cziczo et al. 2004; Pratt et al. 2009; Froyd et al. 2010; Cziczo et al. 2013).

The other means by which INPs can be studied from aircraft platforms (or at high-altitude sites) is to induce nucleation in a portable CFDC (section 2); the concept is to use controlled saturation and temperature to induce ice formation on a subset of the ambient aerosol (DeMott et al. 2010). When the chambers are utilized in free-tropospheric air masses, the assumption is the particles studied are relevant to cirrus formation (DeMott et al. 2003). One particular example is the work of Chen et al. (1998) who used an ice chamber to induce ice formation on upper-tropospheric aerosol as well as contrail-affected air masses. Ice crystals were separated and sublimated with the residuals collected for offline analysis using EM.

2. Measurements methods

a. Ice nucleation chambers

No single chamber has been developed to investigate all ice nucleation mechanisms or the full terrestrial temperature range; chambers are therefore designed to study specific ice nucleation mechanisms and temperature ranges (DeMott et al. 2011). As shown in Tables 8-2 and 8-3, these chambers tend to fall into three broad categories: 1) large chambers in fixed laboratories that accept collected or prepared samples,

2) offline chambers that expose collected or prepared samples to low temperature and ice saturated conditions, and 3) portable chambers for both field and laboratory use.

The main purpose of a cloud chamber is to provide a controlled water vapor content and temperature at which particles can nucleate ice. Aerosol size, concentration, residence time, and composition are then varied so that the ice nucleation onset or frozen fractions can be determined. Note that in some instruments care is taken to be at supersaturated conditions continuously while the temperature is changed [e.g., Leipzig aerosol cloud interaction simulator (LACIS), immersion mode cooling chamber (IMCA); note acronyms defined in Tables 8-1–8-3] while in others the temperature is constant and RH is varied (e.g., most CFDCs and some cold-stage instruments). A subset of chambers, for example, those that use expansion of the air parcel, allow both parameters to be varied at the same time [e.g., aerosol interaction and dynamics in the atmosphere (AIDA)].

For the laboratory chambers, particles are typically directly injected into the cell, with the exception of vacuum chamber (VC) and cold stage (CS), where particles are deposited on a substrate. Droplets with particles immersed are kept within the instruments during immersion freezing experiments conducted in a differential scanning calorimeter (DSC), wind tunnel (WT), optical trap (OT), or electrodynamic balance (EDB). In contrast, in continuous flow instruments [such the LACIS, Zurich ice nucleation chamber (ZINC), portable ice nucleation chamber (PINC), IMCA, portable immersion mode cooling chamber (PIMCA), contact ice nucleation chamber (CINC), Manchester ice cloud chamber (MICC), spectrometer ice nuclei (SPIN), collision ice nucleation chamber (CLINCH), and Massachusetts Institute of Technology–collision efficiency chamber (MIT-CEC) or the WT, EDB, DSC, and OT] the particles pass through the instruments during the experiments. Since particle size (surface area) has been shown to play a role in ice activity there has been a shift to monodisperse studies (i.e., use of mobility selection before the chamber).

The primary goal of the detection system of most cloud chambers is quantification of ice crystals. A secondary goal, discussed in the next sections, is often compositional analysis. To quantify ice crystal number, most instruments use an optical system to either directly capture images of ice crystals or determine number by means of incidents of light scattering from a continuous laser beam at the terminus of the chamber. More sophisticated optical systems that use laser depolarization to distinguish between ice crystals, liquid droplets, and unactivated aerosol particles are now also in use.

b. Separation techniques

The measurement of IRs involves the use of a CVI, first described by Ogren et al. (1985) for aircraft

TABLE 8-2. Examples of laboratory-based contemporary instrumentation to study ice nucleation. Homogeneous freezing (Ho), deposition nucleation (DE), immersion freezing (IM), condensation freezing (CD), contact freezing (CT).

Type of instrument	Abbreviation	Full name	Freezing mode	Type of analysis	References
Chamber	AIDA	Aerosol interaction and dynamics in the atmosphere	Ho, DE, IM, CD	Online	Möhler et al. (2003)
	ZINC	Zurich ice nucleation chamber	Ho, DE, CD, IM	Online	Stetzer et al. (2008)
	LACIS	Leipzig aerosol cloud interaction simulator	Ho, IM	Online	Hartmann et al. (2011)
	MICC	Manchester ice cloud chamber	Ho, DE, IM	Online	Connolly et al. (2012)
	IMCA	Immersion mode cooling chamber	Ho, IM	Online	Lüönd et al. (2010)
	CLINCH	Collision ice nucleation chamber	Ho, CT	Online	Ladino et al. (2011)
	CINC	Contact ice nucleation chamber	Ho, CT	Online	Niehaus et al. (2014)
	MIT-CEC	Massachusetts Institute of Technology–collision efficiency chamber	Ho, CT	Online	Ardon-Dryer et al. (2015)
	WT	Wind tunnel	Ho, DE, IM, CD, CT	Online	Diehl et al. (2011)
Cell	EDB	Electrodynamic balance	Ho, IM, CT	Online	Davis (1997); Hoffmann et al. (2013a,b)
	VC	Vacuum chamber	Ho, DE	Online	Shilling et al. (2006)
	DSC	Differential scanning calorimeter	Ho, IM	Online	Zuberi et al. (2001)
	μl-NIPI	Microlitre nucleation by immersed particle instrument	Ho, IM	Online	Whale et al. (2015)
	CSU-IS	Colorado State University–immersion mode ice spectrometer	Ho, IM	Online	Hill et al. (2014)
	NC State-CS	Cold-stage-supported droplet assay	Ho, IM	Online	Wright and Petters (2013)
	CS	Cold stage	Ho, DE, CD, IM	Online and Offline	Koop et al. (1998); Durant and Shaw (2005)
	BINARY	Bielefeld ice nucleation array	Ho, IM	Online	Budke and Koop (2015)
	OT	Optical trap	Ho, CT	Online	Davis et al. (2015)

applications, where a controlled airflow is blown out of the CVI inlet tip. Smaller interstitial particles are decelerated, stopped, and rejected, whereas larger cloud particles can overcome the counterflow and are impacted into a dry, particle-free flow. The condensed phase of the collected cloud particles is evaporated, releasing the residuals. The CVI separation is only based on inertia and does not differentiate between droplets and ice.

1) AIRCRAFT-BASED INLETS

The deployment of aircraft CVI inlets in cirrus has been used to separate IRs from ambient aerosol because of the absence of droplets in these completely glaciated clouds (e.g., Cziczo et al. 2004, 2013; Froyd et al. 2010; Heintzenberg et al. 1996; Seifert et al. 2004; Stith et al. 2011; Twohy and Gandrud 1998; Twohy and Poellot 2005). The lower cut size of the transmitted particles for a given CVI design depends on the aircraft velocity and the magnitude of the counterflow, with typical cut sizes on the order of a few micrometers aerodynamic diameter (Anderson et al. 1993; Noone et al. 1988; Twohy et al. 2003). Much less discussed in the literature is the upper cutoff diameter of a

CVI. In general, because of geometrical and flow rate limitations, only crystals up to a size of $50\,\mu m$ can be stopped and sublimated without impaction to a wall surface inside traditional CVI inlets (Cziczo and Froyd 2014). As Cziczo and Froyd (2014) point out, cirrus and ice clouds often contain crystals larger than $50\,\mu m$, which means that only the small size fraction has, to date, been sampled. Moreover, the larger crystals that cannot be stopped impact onto internal surfaces; creating artifacts (see section 3b). A further artifact, which is also relevant for ground-based CVI inlets, is the unintentional transmission of interstitial particles below the CVI cut size due to collision, coalescence, or riding the wake of ice particles (Pekour and Cziczo 2011).

2) GROUND-BASED INLETS

Because of the lower altitudes of mountain sites, ground-based inlets are typically operated in MPC conditions and therefore face the additional challenge of cloud phase separation. Since cloud droplets are of a similar aerodynamic size as small crystals, a traditional CVI is insufficient. As described in section 1b, two CVI-based separation techniques (Ice-CVI and ISI) have

TABLE 8-3. Examples of portable instruments (field and laboratory) to study ice nucleation. N_{CCN} is the number concentration of ambient CCN at the sampling location.

Type of instrument	Abbreviation	Full name	Freezing mode	Type of analysis	INP sensitivity (L^{-1})	References
Chamber	PINC	Portable ice nucleation chamber	Ho, DE, CD, IM	Online	0.1	Chou et al. (2011)
	PIMCA	Portable immersion mode cooling chamber	Ho, IM	Online	$0.1*N_{CCN}/L$	Kohn et al. (2016)
	SPIN	Spectrometer for ice nuclei	Ho, DE, IM, CD	Online	1.0	Garimella et al. (2016)
	CSU-CFDC	Colorado State University–continuous flow diffusion chamber	Ho, DE, CD, IM	Online	0.01	Rogers (1988); Rogers et al. (2001)
	UT-CFDC	University of Toronto–continuous flow diffusion chamber	Ho, DE, CD	Online	0.01	Kanji and Abbatt (2009)
	FINCH	Fast ice nucleation chamber	IM, DE, CD	Online	0.01	Bundke et al. (2008)
	TGDC	Temperature gradient diffusion chamber	Ho, DE, CD	Online	0.01	Bailey and Hallett (2002)
	FRIDGE	Frankfurt Ice Deposition Freezing Experiment	IM, CD, DE	Offline	0.01	Bundke et al. (2008)
		Mixing cloud chamber	DE	Offline	0.01	López and Ávila (2013)
	CS (DFT)	Cold stage	Ho, DE, CT, IM	Offline	0.01	Knopf et al. (2010); Mason et al. (2015a)
Cell	DFA	Drop freezing array	Ho, IM	Offline	$1.0e^{-6}$	Bigg (1953); Conen et al. (2012)

been developed for ground-based use. Both inlets use a series of additional components to extract small (5–20 μm) crystals from MPCs.

The Ice-CVI is mounted vertically. Air is sampled through an omnidirectional inlet, which reduces transmission of cloud particles larger than 50 μm (Noone et al. 1992). A virtual impactor downstream removes cloud particles larger than 20 μm. Phase is separated by a two-stage preimpactor (cutoff diameters 10 and 4 μm), where supercooled drops freeze on the impaction plates while crystals bounce off (Tenberken-Pötzsch et al. 2000). The flow is then directed into a conventional CVI (Mertes et al. 2001), where interstitial particles below 5 μm are removed.

In the ISI droplets are removed from the sample flow. This is carried out via the Wegener–Bergeron–Findeisen process, in a so-called droplet evaporation unit (DEU), a chamber with ice-coated inner walls that induce droplet evaporation via the difference in saturation vapor pressures over water and ice. Directly upstream and downstream of the DEU, optical particle size spectrometers count and size cloud particles contained in the sample flow. The phase and habit of cloud particles transmitted through the DEU are ascertained using a particle phase discriminator (Kaye et al. 2008; Vochezer et al. 2016) and interstitial particles are removed from the sample flow using a pumped counterflow virtual impactor (PCVI; Boulter et al. 2006), with a cutoff size of ~5 μm (Kupiszewski et al. 2015).

Both the Ice-CVI and ISI inlet systems have limitations and may suffer from sampling artifacts. The two systems sample through omnidirectional inlets on which crystals could shatter; the released fragments could then make it through the system. The use of impaction plates in the Ice-CVI could produce additional shatter and potential abrasion of material from the plate surfaces, although the kinetic energy of ice under these conditions has been shown to be low (Vidaurre and Hallett 2009). Comparisons of Ice-CVI IR and small ice particle concentrations are similar and suggest minimal artifacts (Kupiszewski et al. 2016; Mertes et al. 2007). The ISI is known to partially evaporate ice crystals within the inlet, thereby leading to rejection of some IRs (Kupiszewski et al. 2015). Another limitation of both inlet systems is the inability to distinguish between primary and secondary ice.

c. Analysis of INPs with microscopy and other optical techniques

INP surface topography, surface area, and other physical and chemical characteristics have been probed using optical and other microscopy techniques. In some cases the technique [e.g., scanning EM (SEM)] can be destructive and/or alter the particle. Less destructive methods can be used to probe the physical and chemical properties of potential INPs before or after subjecting those particles to freezing conditions. A homogeneous aerosol population can also be split between independent freezing and aerosol characterization experiments to
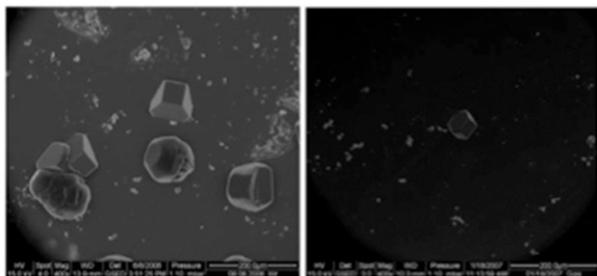
Fig. 8-2. Electron micrographs of ice crystals formed by deposition ice nucleation on a small fraction of mineral dust particles [(left) illite; (right) gypsum] within an ESEM (Zimmermann et al. 2007).

prevent experimental artifacts from influencing subsequent experiments. The techniques discussed in this section generally require that the particle is stationary, which is most frequently accomplished by depositing the particle onto a "cold stage" or an EM "grid" (Fig. 8-2).

Optical microscopy, sensitive to supermicrometer sizes, is typically used to determine when freezing has occurred. EM, with higher resolution, is typically used to determine surface area and topography (Hoffmann et al. 2013a). Limitations of SEM are exposure of the sample to vacuum (thereby potentially losing volatile material) and metallic coating required for samples with low electrical conductivity. Nevertheless, INPs of many different types have been analyzed in the laboratory using SEM (Alpert et al. 2011; Hiranuma et al. 2015a; Shilling et al. 2006; China et al. 2015). Cirrus IRs containing mineral dust, metallic particles, soot, and biological material have also been analyzed by SEM (Cziczo et al. 2013).

The field emission gun (FEG-SEM) technique can overcome problems resulting from low electrical conductivity of sample materials due to the smaller electron beam spot size used. Environmental SEM (ESEM) utilizes differential pumping of the region near the sample and the electron gun, and the higher pressure near the sample allows for electrical discharge while also preventing evaporation of volatile material. Ambient multicomponent aerosol, volcanic ash, and mineral dust INPs have been characterized using ESEM (Hoffmann et al. 2013a; Knopf et al. 2010; Wang et al. 2012a,b), as have IRs collected from orographic MPCs and cirrus (Ebert et al. 2011). By adding a cold-stage and carefully controlling humidity and temperature, ice nucleation experiments can take place within an ESEM chamber (Zimmermann et al. 2007).

Transmission (or tunneling) EM (TEM) has resolving power that can surpass SEM, and has been used to investigate very fine structures ($\sim$10 nm). This capability has been used to identify surface defects and morphology of mineral dust and soot (Freedman 2015; Niedermeier et al. 2011; Sihvonen et al. 2014; China et al. 2015; Zolles et al. 2015) as well as internally mixed organic/inorganic INPs (Veghte et al. 2014). Phase and crystal lattice information at sub-10 nm can be obtained using fast Fourier transformation (FFT) analysis of high-resolution TEM images (Ebert et al. 2011). TEM has also been used to analyze cirrus IRs (Heintzenberg et al. 1996; Stith et al. 2011; Twohy and Poellot 2005; Twohy and Gandrud 1998).

Elemental composition and mixing state of INPs can be determined through energy-dispersive X-ray spectroscopy (EDX), which can be added to an EM instrument (Broadley et al. 2012; Ebert et al. 2011; Heintzenberg et al. 1996; Hiranuma et al. 2015a; Hoffmann et al. 2013b; Knopf et al. 2010; Stith et al. 2011; Twohy and Poellot 2005; Twohy and Gandrud 1998; Wang et al. 2012b; Zimmermann et al. 2007; Zolles et al. 2015).

Scanning transmission X-ray microscopy (STXM) near-edge absorption fine structure spectroscopy (NEXAFS) is used in the analysis of thin-film polymers and to provide chemical functionality relevant for biogenic and organic INPs (Knopf et al. 2010; Moffet et al. 2010; Wang et al. 2012a; Wilson et al. 2015).

Other tools to characterize INPs include Raman spectroscopy, fluorescence microscopy, Fourier transform infrared (FTIR) spectroscopy, attenuated total reflectance FTIR (ATR-FTIR), elastic X-ray diffraction (XRD), and powder XRD (Alpert et al. 2011; Baustian et al. 2013; Broadley et al. 2012; Brooks et al. 2014; Freedman 2015; Hiranuma et al. 2015b; Marcolli 2014; Mason et al. 2015b; Schill et al. 2014; Shilling et al. 2006; Sihvonen et al. 2014; Wise et al. 2012; Zolles et al. 2015).

d. Mass spectrometry of ice nucleating particles

Single-particle mass spectrometers (SPMSs) have been used since the early 1990s for the study of particles. Reviewed by Murphy (2007), the SPMS allows for the determination of single-particle chemical composition, typically of all aerosol components, both in situ and in real time. Modern SPMS instruments focus particles using an aerodynamic inlet and particles are detected and sized using scattered light as they pass through one or two laser beams set a fixed distance apart. Because of the optical detection step, SPMSs are limited to a lower size threshold, typically $\sim$150-nm geometric diameter particles that scatter sufficient light (Murphy 2007). It should be noted that this remains below the expected INP size mode (DeMott et al. 2010). A second laser, typically in the near UV, is fired to ablate the particle and ionize that material. Extracted ions are separated in single- or dual-polarity time-of-flight (ToF) mass spectrometers, thereby producing a complete mass spectrum on a single-particle basis. SPMS is generally considered

qualitative since signal is affected by the particle matrix and instrumental variability. Since its first airborne deployment for analysis of cirrus residuals in the 2001 CRYSTAL-FACE study by Cziczo et al. (2004), SPMS has become the most common technique for IRs analysis since (Cziczo et al. 2004; Pratt et al. 2009; Froyd et al. 2010; Cziczo et al. 2013).

3. Uncertainties and limitations of contemporary measurements

a. Ice nucleation chambers

Most of the available portable online INP counters are limited in operation to temperatures relevant for MPC conditions ($>-40°$C). Lower sampling temperatures ($-40°$ to $-60°$C) would require chamber cold walls to be cooled to $\sim-60°$C and lower, which is challenging to achieve. The focus on warmer temperatures, albeit circumstantial, means there is a gap in knowledge about INP concentrations at cirrus conditions. On the warmer end, CFDCs are limited to sampling temperatures $<-8°$C since the warm wall temperatures would approach close to $0°$C, resulting in melting of the ice layer.

CFDCs require human intervention for icing the chamber walls, a semiautomated procedure at best, limiting their use in continuous monitoring applications. Additionally, they have to be reiced after a few hours because of frost formation on the cold wall (Rogers et al. 2001; Chou et al. 2011). This can be extended somewhat, to ~12 h, in horizontally oriented chambers (Kanji and Abbatt 2009).

CFDCs require laminar flow conditions, resulting in low sample flow rates (~1 lpm). The result of atmospheric measurements in remote areas at the higher-than-cirrus temperature range where CFDCs are most effective is that INP concentrations are often $<1\,L^{-1}$. This then means longer sampling times are necessary for statistical significance. An exception is the fast ice nucleation chamber (FINCH), a turbulent mixing flow chamber that samples 5–10 lpm of ambient air (Worringen et al. 2015; Bundke et al. 2008). Offline techniques that can use higher flow rates (>20 lpm) to impact particles on substrates are also important for an increase of signal (Mason et al. 2015a,b).

CS and DFA techniques have the advantage of a low limit of detection (LOD) but require aerosol sampling and storage prior to ice nucleation analysis. It is not clear if effects of sample handling, storage, and impaction of particles onto substrates exist on the particle structure and morphology. Longer sampling times are typically necessary (>5 h) for size-resolved collections onto filters (Mason et al. 2015a; Wang et al. 2012b).

These limitations illustrate the need for higher instrument sensitivity in remote locations where the INP concentration is low ($<1\,L^{-1}$). Boose et al. (2016) showed that this requires accurate determination of signal to noise and LOD; reporting only INP concentrations $>$ LOD without reporting the frequency of measurements that fall below LOD can result in a significant overestimate of INP for a given location.

Another uncertainty is the determination of ice nucleation rate often achieved by using the residence time of particles in chambers. Since this time includes equilibration, nucleation, and growth, the nucleation rate is necessarily a lower limit (Archuleta et al. 2005; Kanji and Abbatt 2010). This can be overcome in static chambers with high cooling rates if the time between ice nucleation and growth to detectable sizes is small relative to the time particles are exposed to given temperature and RH condition.

Although the EDB is a powerful technique to study different ice nucleation processes such as contact freezing or ice multiplication, and their experiments allow for long experimental time scales, it requires a large number of electrical charges on droplet surfaces for levitation (Hoffmann et al. 2013a). The effect of charge on the freezing process remains to be fully considered. For example, the excess or scarcity of electrical charges can substantially change the collection efficiencies between aerosol particles and cloud droplets, affecting the efficiency of contact freezing (Ladino et al. 2013; Ardon-Dryer et al. 2015).

The use of polydisperse aerosol samples has inhibited the quantification of freezing efficiency in some instruments, such as the wind tunnel, EDB, or a dynamic CS (Ladino et al. 2013). Methods employing monodisperse particles also need to be considered carefully since they can lead to an overestimation of ice nucleation active site densities (INAS) if corrections for multiply charged particles are not applied (Hartmann et al. 2016). In general, measurements can be improved when accurate size distributions are acquired.

For CS methods in deposition and immersion nucleation, coagulation of smaller particles or the use of larger particles up to 10-μm may limit the application of the ice nucleation data generated (Eastwood et al. 2008; Kanji and Abbatt 2006). While large aerosols have been shown to undergo long-range transport (Young et al. 2016), they may not bear atmospheric relevance for ice cloud formation at the upper limit of the investigated particle sizes since they are rare at cirrus altitudes.

Contact and immersion freezing studies conducted with EDB and WT experiments use droplet sizes from 60 to 350 μm (Hoffmann et al. 2013a,b; Diehl et al. 2014). These may not be representative of ice nucleation processes occurring in typical cloud droplets of $\sim20\,\mu$m. In contact freezing studies, low collision efficiencies

pose a significant challenge to determining atmospheric relevance (Ladino et al. 2013). Although laboratory studies have shown that contact freezing is an efficient ice nucleation mechanism, it remains necessary to demonstrate relevance in clouds to understand if it competes with other freezing mechanisms.

b. Inertial separation and inlet artifacts

It has now been demonstrated that artifacts are produced by the collision of ice crystals with aircraft and inlet surfaces (Murphy et al. 2004). The reason for this is that ice crystals and large droplets have significant inertia and do not follow gas flow lines (Korolev and Isaac 2005). A surface impaction is not necessary; ice crystals may also break up upon the deceleration required for sampling (Pekour and Cziczo 2011). The generation of artifacts can best be visualized as crystals breaking into multiple fragments and/or the pitting of surfaces by ice impact (Korolev and Isaac 2005; Murphy et al. 2004).

Cziczo and Froyd (2014) gave a comprehensive account of the various inlet artifacts that include, but are not limited to, 1) inlet material, 2) aircraft material (e.g., paint), 3) combinations of these with real IRs, and 4) liberation of particles that were previously deposited on the inlet surface. Cziczo and Froyd (2014) noted that artifact content most likely went unnoticed in pre-SPMS composition analyses. Evidence supporting the generation of artifacts by ice impact have also been provided by EM: Kojima et al. (2004) detected abundant aluminum-, silicon-, and zinc-containing particles, which were suggested to be aircraft paint chipped by ice crystals. Perring et al. (2013) showed a black carbon artifact that appeared in a forward-facing (but not rear-facing) inlet when cirrus ice was present.

As a result of these observations, modern CVI inlets are constructed with distinct materials that lend an ability to detect artifacts. These include titanium (Stith et al. 2011) and gold (Froyd et al. 2010) as well as design elements such as orthogonal pickoff (Cziczo et al. 2013) that minimize artifact concentration.

4. Challenges to improving observations

There are less than five aircraft-capable ice chambers in existence at the publication of this monograph. This limitation has a direct impact on the ability of our community to understand the spatial and temporal variability of INPs. The SPMSs currently in use for both mountaintop and airborne studies of INPs are of a similarly limited number. The result is that many flight or deployment opportunities go unrealized not because of a lack of interest but because of a lack of instrumentation.

As mentioned in the previous sections, the CVI technique has allowed for investigation of IR properties for over two decades. Airborne inlets are, to date, inertial separation systems only because of the complexity, mass, and size limitations of phase discrimination in the Ice-CVI and ISI. Furthermore, airborne CVIs are limited in upper cutpoint by the stopping distance of large ice at aircraft speeds. This has resulted in (often unrealized) artifact generation as well as no current information on the composition of IRs from crystals larger than ~50-μm diameter (Cziczo and Froyd 2014).

A concerted effort toward reporting global INP concentrations has been suggested since the 1950s but never realized. Using a suite of methods/instruments at specific locations, this challenging task is now realizable with sufficient instrumentation and funding. Models are currently limited by a lack of data and this, in turn, limits our ability to correctly predict ice cloud formation and radiative effects (Hoose and Möhler 2012).

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