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Chapter 1

Overview of Ice Nucleating Particles

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ABSTRACT

Ice particle formation in tropospheric clouds significantly changes cloud radiative and microphysical properties. Ice nucleation in the troposphere via homogeneous freezing occurs at temperatures lower than −38°C and relative humidity with respect to ice above 140%. In the absence of these conditions, ice formation can proceed via heterogeneous nucleation aided by aerosol particles known as ice nucleating particles (INPs). In this chapter, new developments in identifying the heterogeneous freezing mechanisms, atmospheric relevance, uncertainties, and unknowns about INPs are described. The change in conventional wisdom regarding the requirements of INPs as new studies discover physical and chemical properties of these particles is explained. INP sources and known reasons for their ice nucleating properties are presented. The need for more studies to systematically identify particle properties that facilitate ice nucleation is highlighted. The atmospheric relevance of long-range transport, aerosol aging, and coating studies (in the laboratory) of INPs are also presented. Possible mechanisms for processes that change the ice nucleating potential of INPs and the corresponding challenges in understanding and applying these in models are discussed. How primary ice nucleation affects total ice crystal number concentrations in clouds and the discrepancy between INP concentrations and ice crystal number concentrations are presented. Finally, limitations of parameterizing INPs and of models in representing known and unknown processes related to heterogeneous ice nucleation processes are discussed.

1. Relevance of atmospheric ice particles and ice nucleation

Atmospheric ice particles play a dominant role in determining the physical properties of clouds and the chemical composition of the troposphere by exerting enormous influence on physical processes such as radiative transfer, precipitation, and cloud electrification (Cantrell and Heymsfield 2005). Ice particles also promote reactive heterogeneous chemistry, scavenge semivolatile gas-phase and acidic trace gas species, and thereby influence tropospheric composition (Abbatt 2003). For example, the quantity of ice condensate is linked to the water vapor budget in the upper troposphere where gas-phase water is an especially active greenhouse gas (Lindzen 1990). Ice crystals change cloud properties in both precipitating and nonprecipitating glaciated clouds. In mixed-phase clouds (MPCs) the role of ice crystals is particularly important because ice can influence the supercooled liquid water content through the Wegener–Bergeron–Findeisen process (Korolev 2007; Korolev and Field 2008). Most precipitation in clouds initiates via the ice phase (Lau and Wu 2003; Lohmann and Feichter 2005) especially over land

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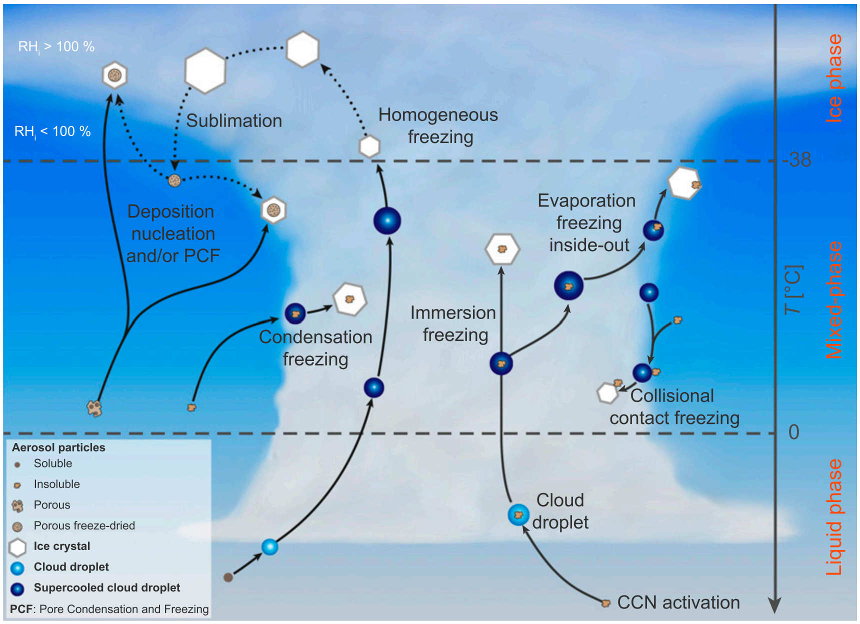

FIG. 1-1. Schematic depicting known primary ice nucleation pathways possible in the atmosphere.

(Mülmenstädt et al. 2015), which significantly influences the hydrological cycle and determines cloud lifetime (Rogers and Yau 1989). In MPCs, forecasting supercooled liquid is crucial because of its hazard in aircraft icing (Cober et al. 2001; Cober and Isaac 2012; Rasmussen et al. 2006; Siebesma et al. 2009).

To predict the impact of the above processes and constrain estimates of the cloud radiation budget, it is imperative to understand the initiation and evolution of ice formation in the atmosphere. The goal of this chapter is to mark the progress made over the last decade but with a focus on the last five years, in understanding which physical and chemical properties of tropospheric aerosol contribute to their role as ice nucleating particles (INPs; sections 3–5). Focus is placed on ice formation on solid aerosol particles via heterogeneous ice nucleation (IN) mechanisms (see section 2) rather than homogeneous freezing of liquid aerosol particles, which is discussed in Heymsfield et al. (2017, chapter 2). Finally we present the challenges that exist in understanding the role of primary IN to microphysics and modeling of INPs in the troposphere (sections 6 and 7).

2. Heterogeneous ice nucleation: A general description

Heterogeneous IN from the parent phase (liquid or gas) occurs when conditions such as temperature, relative humidity, and a surface for nucleation (like an INP) provide energetically favorable conditions for this activated process. Heterogeneous classical nucleation theory (CNT) supposes that the energy of forming a new daughter phase (ice) versus a critical embryo (from a molecular cluster) remaining in equilibrium with the parent phase may be scaled by a foreign surface like that of an INP [see section 7a(2) for more details]. Primary ice formation in the atmosphere at temperature (T) > -38°C occurs only when aided by an INP, which lowers the energy barrier that should be overcome for the formation of the critical ice embryo. Ice nucleating particles can also aid ice formation at $T < -38$°C with a nucleation rate competitive enough when relative humidity with respect to ice, $\mathrm{RH}_i \lesssim 140\%–150\%$. Above this RH_i, the higher nucleation rate of homogeneous freezing (see Fig. 1-1) of solute-containing particles (see Heymsfield et al. 2017, chapter 2) readily outcompetes heterogeneous freezing. At lower temperatures ($T < -75$°C) the heterogeneous freezing description based on activation energy only (contact angle) can result in overlooking the importance of a kinetic parameter [see $\mathcal{K}$ in section 7a(2)], which has been shown to play an important role in the initial ice cluster formation (Laaksonen 2015). Heterogeneous IN is based on the single idea of an INP lowering the energy barrier for IN by stabilizing a critical embryo but is observed (in atmospheric and laboratory measurements) via different pathways as discussed in section 2a below. In section 2b, the relevance of heterogeneous IN in the cirrus cloud regime is briefly discussed and covered in more detail in Heymsfield et al. (2017, chapter 2). This section ends with discussing the INP prerequisites for heterogeneous IN (see section 2c).

a. *Modes of heterogeneous ice nucleation and their relevance in mixed-phase clouds*

Historically, definitions of heterogeneous IN modes have differed and perceptions might change in the future. Herein the descriptions are based on Vali et al. (2015), which was the product of an open discussion and debate during the peer-review process in the journal *Atmospheric Physics and Chemistry Discussions* between a number of research groups [see the interactive discussion for Vali et al. (2015) on the journal website]. The different pathways discussed below are depicted in Fig. 1-1.

Deposition ice nucleation is the only heterogeneous IN mechanism where liquid water is presumed to be absent. Ice nucleates from supersaturated vapor with respect to ice ($RH_i > 100\%$) on an INP directly. Recently, Marcolli (2014) suggested that observations interpreted as showing deposition IN could also be pore condensation and freezing (PCF; see Fig. 1-1) occurring by condensation of water in cavities found on the surfaces of INPs because of the "inverse Kelvin" effect at $RH_i < 100\%$ followed by homogeneous freezing at sufficiently low temperatures ($T < -38°C$). This mechanism was recently observed by Wagner et al. (2016), where it was called preactivation. In the pores of particles, ice formed homogeneously at sufficiently low temperatures. In decreasing $RH_i < 100\%$, ice was retained up to −13°C and induced macroscopic ice growth as soon as RH_i was increased to values slightly above saturation (see dotted pathways in Fig. 1-1). It was estimated that this effect takes place for pore sizes of 5–8 nm. Sullivan et al. (2010a) examined Arizona Test Dust (ATD) particles exposed to nitric acid (HNO_3) and observed a sharp increase in their ice nucleating ability just below water saturation at $RH_w \sim 97\%$. They interpreted that as a shift from deposition nucleation to a mechanism that includes the formation of liquid water (condensation/immersion freezing mechanism, see below). It is therefore unclear to what extent data reported as deposition IN in the past truly occur directly via the vapor phase, and what role this plays for interpretation of atmospheric processes. This mechanism is not expected to be significant for ice formation in MPCs where INPs are expected to be activated to droplets first (Ansmann et al. 2008), but it might still be important for cirrus clouds (Cziczo et al. 2013).

Contact freezing is initiated when an INP approaches the air–water interface from the outside of a droplet (e.g., via a collision, Fig. 1-1), however, this can also occur from "inside out," as has been observed when an INP touches the droplet surface from within the droplet, as depicted in Fig. 1-1 (Durant and Shaw 2005; Fornea et al. 2009; Shaw et al. 2005). Recently, several new techniques have been deployed to examine contact freezing (Hoffmann et al. 2013a; Ladino et al. 2011; Niehaus et al. 2014). Contact freezing probability has been reported to be proportional to the surface area of the INP (Hoffmann et al. 2013a,b; Nagare et al. 2016), challenging the concept that such freezing is triggered by the first point of contact between droplet and INP. However, the same studies show that contact-initiated freezing efficiency dominates over immersion freezing in the laboratory studies described, thus questioning the involvement of the entire particle in contact freezing. Niehaus and Cantrell (2015) found that contact freezing was also initiated when particles consisting of different soluble substances, which were already deliquesced at their surfaces upon contact, hit a supercooled droplet, that is, impact-initiated contact freezing. Subsequently, the authors reported that INPs active in the contact freezing mode need not be solid albeit with a caveat about the large sizes of the examined droplets ($d > 25$–$150\,\mu m$). This limits the atmospheric relevance to larger wet particles colliding (e.g., rain and drizzle) rather than collisions between cloud droplets and INPs, which would be much smaller than the diameters reported in Niehaus and Cantrell (2015). In summary, evaporation of a droplet could lead to inside-out contact freezing and particle collisions may provide energy from the impact of the INP with the droplet surface for freezing. The frequency with which these two mechanisms occur and hence overall importance of contact freezing in the atmosphere remains poorly understood, but its contribution could be relevant to MPCs (Seifert et al. 2011).

Immersion freezing refers to IN initiated by an INP that becomes immersed in an aqueous solution or water droplet via activation of cloud condensation nuclei (CCN) during liquid cloud formation (see Fig. 1-1). A subset of CCN could also be effective INPs. Immersion freezing is suggested to be most important for MPCs (Ansmann et al. 2008; de Boer et al. 2011; Westbrook and Illingworth 2013). This process has been observed in a large number of studies reported in Murray et al. (2012), with newer ones reported in section 3. It is generally observed when droplets are made directly from suspensions (composed of INPs and water or salt solutions, including natural precipitation samples), as was already done by Bigg (1953). Other methods include activating INPs to droplets prior to freezing, which is achieved, for example, in cloud chambers like the Aerosol Interaction and Dynamics in the Atmosphere (AIDA; Möhler et al. 2003), the flow tube reactor Leipzig Aerosol Cloud Interaction Simulator (LACIS; Hartmann et al. 2011), the immersion flow chamber (Portable) Immersion Mode Cooling Chamber [(P)IMCA; Kohn et al. 2016; Lüönd et al. 2010], and using the droplet freezing technique where water is condensed onto particles on a substrate followed by applying supercooling (e.g., Koop et al. 1998; Mason et al. 2015b). Under high-enough RH_w, immersion freezing can also be measured in continuous flow diffusion chambers (CFDCs; Rogers 1988). Activated fractions of dust INPs measured in a CFDC at $\mathrm{RH}_w = 105\%$ were observed to be within a factor of 2–3 of the frozen fractions observed in immersion freezing measured in the AIDA cloud chamber expansions (DeMott et al. 2015); however, if the comparison were done at higher RH_w, the discrepancy almost disappeared. Similar or better agreement between a CFDC operated at $\mathrm{RH}_w = 105\%$ and the LACIS immersion freezing device is noted by Wex et al. (2014), if measured activated fractions are scaled by instrument residence times under the assumption of steady-state nucleation rates. Additionally, Wex et al. (2014) showed that kaolinite particles coated with nanometer thick soluble material showed no measureable ice nucleating ability at $\mathrm{RH}_w \lesssim 95\%$ and a sharp increase for increasing $\mathrm{RH}_w \sim 100\%$. The measured IN below water saturation could be described by combining immersion freezing parameterizations with concentration-dependent freezing point depression implying the observed freezing at $\mathrm{RH}_w < 100\%$ to be immersion freezing of concentrated solution droplets (Wex et al. 2014). These observations suggest that CFDCs can measure immersion freezing at sufficiently high RH_w, that is, above the deliquescence point of soluble material present on an INP, or at least when all particles are subject to sufficiently high supersaturations (Garimella et al. 2017), which should be expected for $\mathrm{RH}_w \geq 105\%$ (DeMott et al. 2015).

Condensation freezing is often referred to as a separate heterogeneous freezing mode, although historically, only three ice nucleating modes were assumed to exist (Fukuta and Schaller 1982), combining immersion and condensation freezing. The most current definition of condensation freezing is based on freezing being initiated concurrently with the initial formation of liquid on CCN at supercooled temperatures (Vali et al. 2015) as shown in Fig. 1-1. However, Vali et al. (2015) also state that it is not fully established if condensation freezing (on a microscopic scale) is truly different from deposition nucleation or immersion freezing and advise further circumspection for its use as a separate mechanism.

b. *Relevance of heterogeneous ice nucleation for cirrus clouds*

In cirrus clouds (see Heymsfield et al. 2017, chapter 2), both homogeneous (see Fig. 1-1) and heterogeneous IN can occur at $T < -38°\mathrm{C}$ where RH_i can vary above and below 140%–150% ($\mathrm{RH}_{\mathrm{hom}}$), which is the threshold above which homogeneous freezing nucleation rates of cloud and solution droplets are large enough to dominate the freezing process (Spichtinger and Cziczo 2010). Under cirrus cloud conditions, field measurements by DeMott et al. (2003a) and later Cziczo et al. (2013) also reported that homogeneous and heterogeneous IN can occur from the ambient aerosol population as is expected based on numerous theoretical and modeling studies (Haag et al. 2003; Kärcher and Lohmann 2003; Kärcher and Spichtinger 2009; Spichtinger and Cziczo 2010, and references therein). Using the composition and mixing-state measurements of ice residuals as well as RH at which cirrus clouds form, Cziczo et al. (2013) inferred deposition nucleation to be the dominant ice-forming mechanism. Krämer et al. (2016) distinguished between different types of cirrus: first, cirrus clouds that form in air parcels further down in the atmosphere and subsequently uplifted are mostly formed via heterogeneous freezing of liquid drops; second, new in situ cirrus formed at high altitudes, where deposition IN could play a role in addition to homogeneous freezing. Additional information on both cirrus clouds and MPCs can be found in Heymsfield et al. (2017, chapter 2) and Korolev et al. (2017, chapter 5), respectively.

c. *Known prerequisites of ice nucleating particles*

It is still not known with enough detail and certainty which properties make an aerosol particle an INP. Historically, several properties have been proposed to play a role (Pruppacher and Klett 1997), but advances have been made in this regard that challenge conventional wisdom in particular with regard to the requirement to have an insoluble particle or particle with macroscopic structural integrity acting as an INP. In the following, an overview of prerequisites for heterogeneous IN is discussed for insoluble and soluble particles and under the expectation that INPs are exposed to subzero temperatures and a supersaturation with respect to ice. Furthermore, requirements specific to each aerosol particle type are discussed in section 3.

For *insoluble/solid particles* (e.g., mineral dusts), it has been long suggested that IN would occur at certain locations (e.g., lattice mismatches, cracks, hydrophilic sites), an idea that complements the old concept of ice-active sites (Pruppacher and Klett 1997). The probability of the occurrence of such sites has been reported to scale with particle surface area (Archuleta et al. 2005; Kanji and Abbatt 2010; Welti et al. 2009), with Hartmann et al. (2016) showing quantitative agreement. This concept indeed is a base for many INP parameterizations (e.g., Connolly et al. 2009; Niemand et al. 2012). As the sites appear with a finite probability (Niedermeier et al. 2015), smaller particles (e.g., <500 nm) are less likely to act as INPs. However, in Mertes et al. (2007), ~200-nm diameter particles were inferred to make up the majority of all INPs, based on the mode size in atmospheric ice residual number distributions. Functional groups such as −OH (hydroxyl) groups on the surface of an INP being able to hydrogen bond with water molecules can be expected to play a role in promoting IN. In this respect, Kanji et al. (2008) observed that the ice nucleating activity in deposition mode of silica particles could be completely suppressed by functionalization of the −OH groups with $-(CH_2)_7CH_3$ (an octyl chain). To that effect, the work of Freedman (2015) and Sihvonen et al. (2014) suggested that the role of −OH groups on edge sites of aluminosilicate clay minerals are potentially important for IN in the deposition mode. The same studies inferred by forming soluble alunogen $[Al_2(SO_4)_317H_2O]$ products on these particles, that ice nucleation proceeded via condensation/immersion mode. A positive influence on ice nucleation of a lattice match between ordered hexagonal bilayer patches of the active surface has also been proposed via 1) molecular dynamics calculations of graphitic soot (Lupi et al. 2014), and 2) empirical studies of ice nucleation with silver iodide (Vonnegut 1947), dust and volcanic ash particles (Kulkarni et al. 2015a). The microscopic patches of the crystalline plane with (100) orientation, exposed at surface defects such as steps, cracks and cavities have been identified as the preferential ice nucleating sites in K-feldspars (Kiselev et al. 2016). When fully functionalized with hydroxyl groups, this high-energy plane exhibits a strong affinity to the prismatic plane of ice, thus inducing a preferential orientation of ice crystals forming on the surface of the feldspar crystal. However, the extent to which INP properties—that is, lattice structure, size, surface defects, and nature of chemical functional groups—are responsible in relation to each other for initiation of IN and their molecular identity remains to be determined.

For *soluble particles and nanoscale biological fragments*, it has been known for a long time that protein complexes (which belong to macromolecules) embedded in a cell membrane are responsible for IN (Govindarajan and Lindow 1988; Hartmann et al. 2013; Lindow et al. 1982; Turner et al. 1990, 1991). In the context of IN for tropospheric clouds, it was more recently shown that biological ice nucleating active macromolecules (INMs) with sizes of only ~10 nm can separate from their carriers, for example, pollen (Pummer et al. 2012), fungal spores (Fröhlich-Nowoisky et al. 2015), and marine organic aerosol (Wilson et al. 2015) and from organic material in soil dusts (O'Sullivan et al. 2015). The discovery of small INMs questions conventional wisdom that INPs (for ice cloud formation) need to be insoluble, or be above a certain size threshold (Pruppacher and Klett 1997). The insolubility requirement for an INP was also challenged by showing that effloresced ammonium sulfate $[(NH_4)_2SO_4]$ particles (Abbatt et al. 2006) and a variety of solid soluble salts already deliquesced at the surface (Niehaus and Cantrell 2015) can form ice heterogeneously (see section 3h). It was also shown that a single INM alone can induce IN (Augustin et al. 2013; Hartmann et al. 2013) and that differently sized INMs can nucleate ice at different temperatures, where the size of these INMs scales with the size of the critical ice embryo at the respective temperature (Pummer et al. 2015). It should also be mentioned that proteins exist that inhibit freezing of larger ice crystals, known as antifreeze proteins, as described in, for example, Davies (2014). Antifreeze proteins share structural similarities with ice nucleating proteins but are smaller in size (e.g., 8–9 kDa in beetles and moths) compared to ice nucleating proteins (typically >100 kDa to several hundreds of kDa). The observed ice nucleating ability of INMs could be attributed to water molecules arranging around the INM functional groups via hydrogen bonds with −OH and amino ($-NH_2$) groups. Such INMs can be bound to host particles (e.g., mineral or soil dust particles, Augustin-Bauditz et al. 2016; O'Sullivan et al. 2016) and will be difficult to detect but could provide the active site or chemical bond requirement necessary to stabilize ice nucleation. The extent of adsorption of INMs to host particles may scale with the size/surface area of the particles carrying the INMs. However, the IN activity arising from such INMs should not scale with the host particle size for cases where the host particle is probed after the removal of such INMs (in the same T range).

3. Primary sources and types of atmospherically relevant INPs

Primary aerosol particles are emitted into the atmosphere by a large variety of sources at different rates. The most relevant natural sources are deserts, volcanic eruptions, oceans, and vegetation debris, whereas important anthropogenic sources of atmospheric aerosol are particles from agricultural practices, deforestation, biomass burning, transportation, and industrial processes. The main aerosol particle types that can act as INPs are described in the following subsections with a focus on results from the last decade and current gaps in knowledge. The particle types discussed in this section include laboratory studies that investigate highly idealized systems or internally and externally mixed particles that have been sampled from the atmosphere and studied in the laboratory under controlled conditions (see Figs. 1-2 to 1-8). In section 5 we present a summary of atmospheric field measurements (see Fig. 1-10) where we classify the measurements based on known airmass types and sampling location to imply INP source(s). To define the ice nucleation abilities of various aerosol particle species, a

TABLE 1-1. Definitions of metrics used to summarize and discuss ice nucleation results presented in this chapter.

Metric	Definition
AF	$\mathrm{AF} = N_{\mathrm{ice}}/N_{\mathrm{tot}}$, where N_{ice} = no. of ice crystals, N_{tot} = total particle no.
F_{ice}	$F_{\mathrm{ice}} = N_{\mathrm{ice}}/(N_{\mathrm{ice}} + N_{\mathrm{droplets}})$, where N_{droplets} is no. of unfrozen drops
n_s and n_m monodisperse aerosol experiments	$n_s(\#\,\mathrm{cm}^{-2}) = -\ln(1-\mathrm{AF})/A(\mathrm{cm}^2)$; A = surface area of 1 particle $n_m(\#\,\mathrm{mg}^{-1}) = -\ln(1-\mathrm{AF})/m_{\mathrm{INP}}(\mathrm{mg})$; m = mass of 1 particle
n_s and n_m approximation for experiments with polydisperse aerosol valid for AF < 0.1	$-\ln(1-\mathrm{AF}) \cong \mathrm{AF}$; for AF < 0.1, $\Rightarrow n_s(\#\,\mathrm{cm}^{-2}) = \dfrac{\mathrm{AF}}{A(\mathrm{cm}^2)} = \dfrac{N_{\mathrm{ice}}}{N_{\mathrm{tot}} \times A(\mathrm{cm}^2)} = \dfrac{N_{\mathrm{ice}}}{A_{\mathrm{total}}(\mathrm{cm}^2)}$ A_{total} = SA of polydisperse size distribution For n_m, A_{total} is replaced with the equivalent mass distribution
Ice onset	Defined variably, ranging from first appearance of ice to AF of 1 Typical values include AF = 10^{-4}, 10^{-3}, 10^{-2}, and 10^{-1}

number of different metrics are referred to in the text and figures presented. These are defined in Table 1-1 and include 1) ice-active surface site density (n_s), 2) ice-active mass site density (n_m), an analog to n_s but mass equivalent, 3) the median freezing temperature (T_{50}) at which 50% of a droplet population is reported frozen, 4) frozen fraction (F_{ice}) reporting the ratio of frozen droplets to the sum of frozen and unfrozen droplets, 5) activated fraction (AF) reporting the ratio of ice crystals formed to total number of aerosol particles sampled, and 6) ice onset conditions that represent the appearance of a predefined number of ice crystals (ranging from the first observed ice crystal to an AF of 1, e.g., see Fig. 1-3) at given RH and T conditions. Since ice onset is typically defined by an AF, it is not normalized to particle surface area or mass, making it challenging to compare results from different studies. In many older studies this was the only metric reported. For all quantities, an ice-active particle is characterized by the highest possible value of the metric at the highest observed temperature/lowest observed RH. How the data are plotted in the presented figures (i.e., as AF, F_{ice}, n_s, n_m, or as onset) depends on a combination of 1) the metric the authors of the respective papers present and 2) the harmonization of datasets for comparison based on the same metric when possible. The harmonization was only performed if the auxiliary particle information (size, mass, density) that is required was available in the published studies.

a. Mineral and desert dusts

Mineral dust particles are recognized as the most important INP type because of their generally effective ice nucleating ability (Hoose and Möhler 2012; Ladino Moreno et al. 2013; Murray et al. 2012) and their large emission rates of up to 5000 Tg yr^{-1} (Engelstaedter et al. 2006) translating to a global distribution of atmospheric dust (Knippertz and Stuut 2014; Prospero 1999; Prospero et al. 2002). The main sources of dust particles are arid soils or deserts (discussed in this section), volcanoes (see section 3g), and agriculture soils (see section 3e). As shown in Hoose and Möhler (2012), dust particles activate as ice crystals at $T < -15°\mathrm{C}$; however, they readily act as INPs at higher temperatures depending on, among other factors, the type and amount of K-feldspar fraction, particle size, and particle concentration per droplet in the immersion mode (Atkinson et al. 2013; Augustin-Bauditz et al. 2014; Harrison et al. 2016; Peckhaus et al. 2016). Boose et al. (2016c) found up to 5 wt% K-feldspar in four airborne Saharan dust samples whereas Kaufmann et al. (2016) found K-feldspar only in samples collected in Qatar and Antarctica but not in nine other dust samples collected in different deserts worldwide. Knowing the atmospheric abundance but more specifically the available surface area fraction of highly active ice nucleating components of dust, such as K-feldspar, would be necessary to truly evaluate the efficiency of dust as an INP at warmer temperatures ($T > -15°\mathrm{C}$) in the atmosphere. Dust particles are important on a regional scale but can also undergo long-range transport, in many cases influencing ice cloud formation far away from the source. Many studies have shown dust to be the most representative composition of ice residuals collected in orographic wave clouds and cirrus clouds in the upper troposphere (Creamean et al. 2013; Cziczo et al. 2013; DeMott et al. 2003b; Pratt et al. 2009) as well as in cirrus anvils if dust is also present in the boundary layer and convectively transported into the upper troposphere (Cziczo et al. 2004).

Even though it is still unclear what the main reason is for the high ice nucleating activity shown by some types of dust particles, previous studies allow us to better understand this enigma. Archuleta et al. (2005), Welti et al. (2009), and Kanji and Abbatt (2010) found that the ice nucleating activity of dust particles increases with

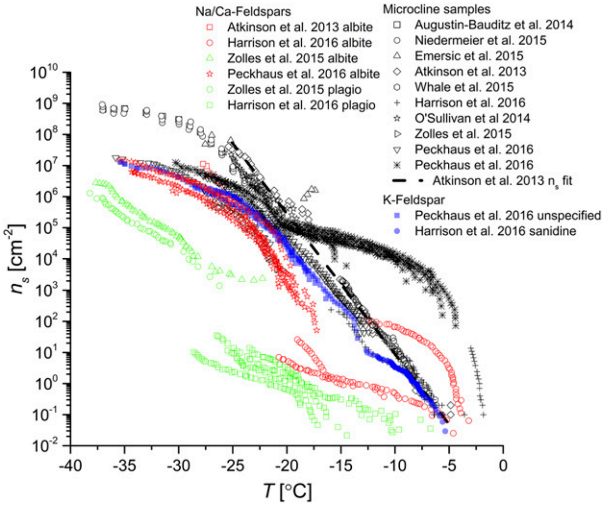

FIG. 1-2. Ice nucleation active site densities n_s as a function of temperature for a variety of feldspar samples. "Unspecified" in the legend refers to the specific K-feldspar mineral phase not being known. Microcline samples have been classified based on a majority of microcline present by %wt and contain minority proportions of other feldspars or minerals. See legend for data from Emersic et al. (2015).

size (i.e., larger surface area). More recently it was found that freshly milled dust might show increased ice nucleating activity compared to aged particles (Hiranuma et al. 2014a; Zolles et al. 2015), and among mineral particles, K-feldspar (possibly microcline, one of the two K-feldspar end members) has been identified as the most ice-active component with the exposed (100) plane promoting ice nucleation preferentially (Kiselev et al. 2016). In Fig. 1-2 we present a summary of feldspar immersion mode IN activity by plotting n_s (see Table 1-1, sections 3 and 7) as a function of temperature. In immersion mode, the ice nucleating efficiency of K-feldspar was first shown by Atkinson et al. (2013) and later confirmed in other studies (Augustin-Bauditz et al. 2014; Zolles et al. 2015) and in deposition mode shown by Yakobi-Hancock et al. (2013) and Zimmermann et al. (2008). Furthermore Harrison et al. (2016) report microcline and albite (Na-feldspar) samples to be active in immersion mode for temperatures as warm as −2° and −4°C, respectively. Similar ice nucleating activity for sanidine (K-feldspar) has been reported in Peckhaus et al. (2016). From the summary of feldspar n_s presented in Fig. 1-2, it can be said that for a given temperature, microcline is generally more IN active compared to other types of feldspar polymorphs. The ice nucleating efficiency in deposition mode is suggested to come from attractions between the charged feldspar crystal lattice and the dipole moment of water resulting in possible attractive ion-dipole forces (Yakobi-Hancock et al. 2013). In the immersion mode, Zolles et al. (2015) suggested that the ice nucleating activity depends on the strength of hydration shells forming around the alkali-metal ions with weaker hydration shells allowing for water molecules to be available to form ice like embryos, whereas Pedevilla et al. (2016) reported that icelike structures are not strictly necessary to nucleate ice. In aluminosilicate clay minerals such as kaolinite, −OH edge groups were inferred to be preferential sites for ice nucleation over the basal plane (Freedman 2015). Preferential nucleation of ice crystals at the edges of stacked kaolinite platelets over the basal plane was also confirmed using electron microscopy studies (Wang et al. 2016). The priority of the IN community should be to quantitatively identify the specific roles of dust ice nucleating particles by elucidating the preferential sites of ice nucleation in dust components given the implication of dust in cloud formation on regional and global scales.

b. *Metals and metal oxides*

Metal oxide particles also form significant components of dust particles but are mainly generated by anthropogenic activities like smelting, aircraft engine ablation, and urban dust. Cziczo et al. (2009b, 2013) found that metallic particles (containing metals such as iron, lead, nickel, and copper) were frequently observed in the ice residues from cirrus clouds. The metal particle efficiency at nucleating ice has been shown to vary as a function of chemical composition. For example, metal oxides such as aluminum oxide, and iron oxide were found to nucleate ice via deposition nucleation at temperatures ranging from −45° to −60°C with IN onsets close to the homogeneous freezing threshold at −45°C (Archuleta et al. 2005). Yakobi-Hancock et al. (2013) also observed a poor ice nucleating ability for pure metals and metal oxides at −40°C. Cziczo et al. (2009b) found that lead-containing particles are among the most efficient INPs of tested metals. Lead was observed in ice residuals collected in different locations such as the Storm Peak Laboratory in Steamboat Springs, Colorado, and the Jungfraujoch in the Swiss Alps (Kamphus et al. 2010). Later on, in a laboratory study Yakobi-Hancock et al. (2013) found that commercially available lead iodide (PbI_2) was a highly active INP in comparison to 23 other samples including clays, metal oxides, and dust particles. This is in contrast to a study by Corbin et al. (2012), who found that the presence of metal-rich particles in the INP population measured at a roadside downtown Toronto, Ontario, Canada, was negligible.

c. *Organics and glassy particles*

Primary organic particles can be, for example, emitted in marine environments, whereas secondary organic aerosol (SOA) particles result from gas-to-particle conversion of volatile organics. Much of the data on

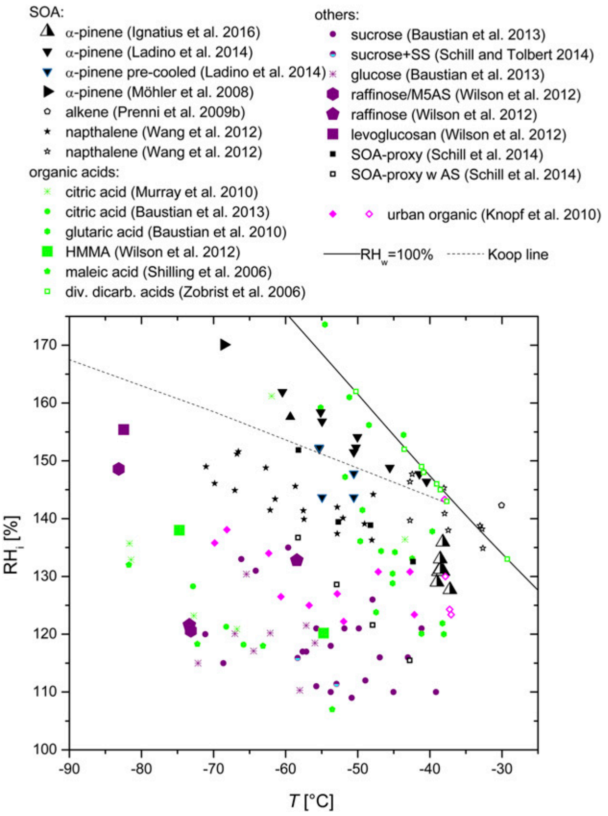

FIG. 1-3. Ice nucleation onset RH$_i$ as a function of temperature for organic particles. Smallest symbol sizes refers to first observed ice or AF $\leq 10^{-4}$ (for majority of the data points) and progressively larger symbols (for Ladino et al. 2014) correspond to AF of 10^{-3} and 10^{-2} for Möhler et al. (2008), with the largest being AF = 0.1 to 0.2 for Wilson et al. (2012) and Ignatius et al. (2016). Open symbols: immersion freezing observed; closed symbols: deposition nucleation; partially open symbols indicate experiments for which either immersion or deposition nucleation could be responsible for ice nucleation. Knopf et al. (2010) data are field samples but as we could not convert them to atmospheric INP concentrations as done in Fig. 1-8, we have included them here. SOA proxy refers to a mix of methylamine and methylglyoxal. AS: $(NH_4)_2SO_4$. Solid line: water saturation based on Murphy and Koop (2005). Dashed line: homogeneous freezing of solution droplets with dry diameter of 500 nm assuming a nucleation rate coefficient of 10^{10} cm^{-3} s^{-1} (Koop et al. 2000).

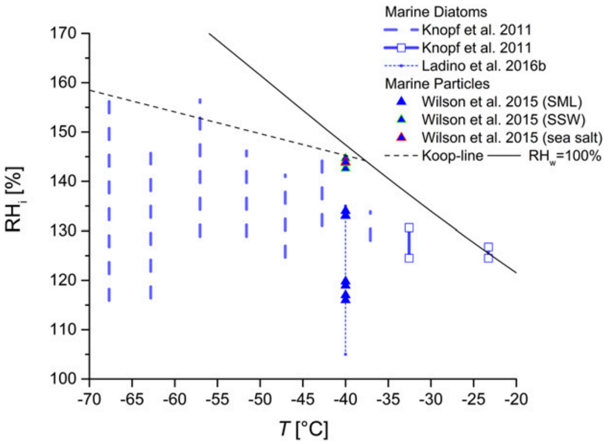

FIG. 1-4. Ice nucleation onset RH$_i$ as a function of temperature for marine particles. Blue dashed lines indicate range of onset RH$_i$ (first observed ice) in which ice nucleation by deposition (or homogeneous freezing) was observed. Open symbols: immersion freezing (AF = 10^{-2}); closed symbols: deposition nucleation (or homogeneous freezing). SML: sea surface microlayer, SSW: subsurface ocean water. AF = 10^{-2} (Wilson et al. 2015) and 10^{-3} (Ladino et al. 2016). Solid and dashed lines as in Fig. 1-3.

IN from the literature (see Fig. 1-3) are based on laboratory studies of idealized organic particles due to the complexity in the characterization of ambient organic particles. Organic material (likely of primary origin) emitted by marine organisms collected from the sea surface microlayer was found to nucleate ice via deposition mode at RH$_i$ < 120% for $T = -40$°C (blue triangles Fig. 1-4), well below the homogeneous freezing threshold, and for T as warm as −10°C in immersion mode (Wilson et al. 2015), as shown by the blue circles and diamonds in Fig. 1-5 (see next section for discussion of bioaerosol). Knopf et al. (2010) found ambient particles coated in SOA collected in Mexico City to be IN active for $T < -33$°C and RH$_i$ ~130% (pink diamonds Fig. 1-3). The results on the ice nucleating ability of laboratory generated SOA particles or complex mixtures of organics are highly varied and summarized as onset of ice nucleation as a function of T in Fig. 1-3. "Pure" organics, such as oxalic acid, citric acid, and maleic acid, were found to promote IN via deposition mode only at $T < -40$°C when amorphous glasslike species form (Baustian et al. 2013; Murray et al. 2010; Shilling et al. 2006; Wilson et al. 2012; Zobrist et al. 2006). Particles composed of a mix of sucrose and sea salt showed similar onsets for deposition IN as pure sucrose and glucose particles at RH$_i$ < RH$_{hom}$ between −50° and −60°C as shown by purple stars and filled circles in Fig. 1-3 (Baustian et al. 2010; Schill and Tolbert 2014). Wang et al. (2012) and Ignatius et al. (2016) found that SOA particles are able to nucleate ice via immersion freezing at $T > -40$°C (black open stars and half open triangles in Fig. 1-3). In the latter study, immersion freezing of the highly viscous SOA is proposed, but the possibilities of deposition nucleation or hygroscopic growth followed by freezing of droplets due to mobilized organic macromolecules in the drop are also considered. In deposition mode, naphthalene SOA (Wang et al. 2012) and a SOA proxy composed of equal parts methylglyoxal/methylamine (Schill et al. 2014) nucleated ice by deposition at $T < -40$°C at RH$_i$ < RH$_{hom}$ (see Fig. 1-3). For $T > -40$°C the SOA proxy particles liquefy before ice formation and the naphthalene SOA particles freeze by immersion via water condensation onto the glassy particles (black open stars Fig. 1-3). When $(NH_4)_2SO_4$ (ammonium sulfate) was added to the SOA proxy, Schill et al. (2014) report immersion freezing (open black squares Fig. 1-3) for $T < -40°C$ at lower RH_i than required for deposition nucleation (filled black squares Fig. 1-3). Ladino et al. (2014) found that for $T < -40°C$, $RH_i > RH_{hom}$ conditions were required for IN of α-pinene SOA particles (Fig. 1-3), which is in contrast to the results from naphthalene and methylglyoxal/methylamine SOA proxy. Last, shown in Fig. 1-3 are data from earlier studies that found SOA particles to be ice inactive at −63°C (Möhler et al. 2008) and −30°C (Prenni et al. 2009b). Determining the freezing mechanism of complex organic mixtures will also be related to the relative time scales of viscosity transitions and ice formation (Lienhard et al. 2015). Therefore, it is not surprising that varied ice nucleating activity of organic particles results from the different types of SOA investigated, variable organic composition, and corresponding viscosity of the aerosol particles and particle-generation methods used. Investigations to understand which property—that is, degree of oxidation, functional group density, mixing, or viscosity/phase—renders secondary organic aerosol components as INPs are lacking.

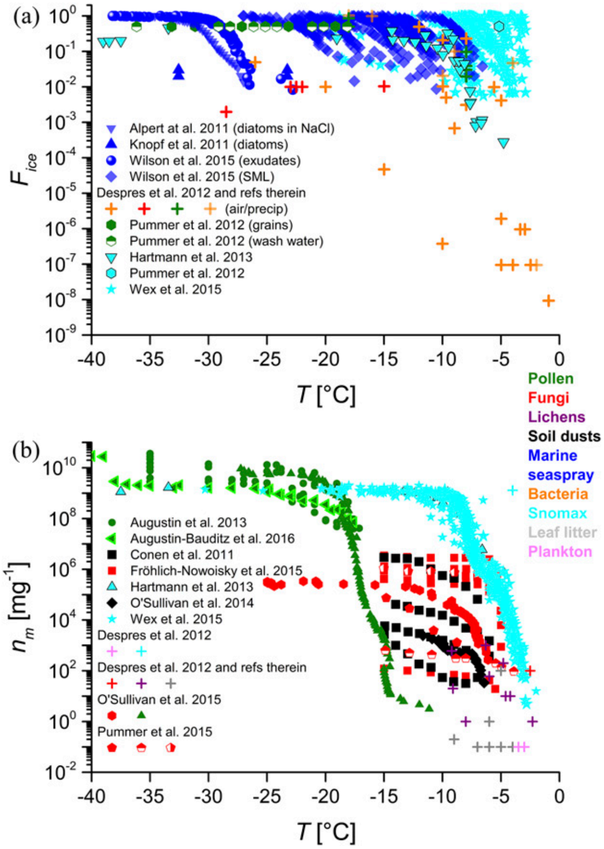

FIG. 1-5. Summary of ice nucleation results of a variety of biological particles. Symbol colors correspond to font color of listed particle type. (a) F_{ice} as a function of particle temperature. (b) Ice nucleation active mass site density (see Table 1-1 and text for definition) n_m as a function of temperature. The n_m values for Augustin et al. (2013) and Augustin-Bauditz et al. (2016) have been derived from data available in the papers. The n_m values for Hartmann et al. (2013) are derived and available in Wex et al. (2015). Pummer et al. (2015) data are for T_{50} of different pollen samples.

d. *Bioaerosols*

Bioaerosol refers to airborne biological particles (e.g., bacteria, fungal spores, pollen, viruses, phytoplankton, lichens, marine exudates, and plant fragments) emitted by biogenic sources such as oceans, vegetation, soils, lakes, and living organisms (Després et al. 2012). Like other aerosol particles, the IN ability varies depending on the type of particle and their atmospheric relevance strongly depends on their tropospheric concentrations. Biological particle signatures have been detected in ice residues sampled from clouds (e.g., Creamean et al. 2013; Pratt et al. 2009) but it remains unclear what their impact on cloud formation is on a regional and global scale. There is a large body of evidence supporting the effective IN ability of some bioaerosols (e.g., Alpert et al. 2011; Augustin et al. 2013; Hiranuma et al. 2014b, 2015; Huffman et al. 2013; Knopf et al. 2011; Mason et al. 2015a; Pandey et al. 2016; Prenni et al. 2013; Pummer et al. 2012; Wex et al. 2015). Using sum-frequency-generation spectroscopy and molecular dynamics simulations Pandey et al. (2016) show that the active sites of the ice nucleation protein (inaZ) found on the outer cell membrane of *Pseudomonas syringae bacteria* feature unique hydrophilic–hydrophobic patterns that promote the ordering of nearby water molecules thus enhancing ice nucleation. In Fig. 1-5a we show F_{ice} as a function of T of a collection of bioaerosol such as *P. syringae* (e.g., Snomax),[1] pollen and particles from the sea surface microlayer all of which freeze at very low to moderate supercooling ($T > -15°C$). Marine diatoms, diatom exudates, fungi, and washing waters from pollen all form ice at $T < -15°C$ (see Fig. 1-5a). However, there is a considerable spread in the data. For example, the Snomax F_{ice} plotted in Fig. 1-5a (cyan stars) are all plotted for the same sample but for different particle sizes and instruments (see Wex et al. 2015 for more details), and show a considerable spread in F_{ice}. This is not surprising as the particle size and concentration of particles in the droplets should influence the freezing temperature and hence F_{ice}. In Fig. 1-5b, we show the same Snomax data

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[1] Snomax is a registered trademark.

(cyan stars) but plotted as $n_m(T)$ (see section 3), which accounts for the mass of the material in the droplets freezing, resulting in very good agreement between the different particle sizes and instrument techniques. This makes n_m a good metric in addition to n_s to compare relative IN abilities of different particle types by normalizing to the mass concentrations. In particular, this is true for INPs where a surface is not defined and thus impossible to obtain a geometric surface area as is the case with INMs from biological particles. Recently it was shown that with sample storage age (as dry pellets), the ice nucleating activity of Snomax deteriorated, therefore necessitating further caution in considering the batch and age of the Snomax when using it as a reference sample in the IN community (Polen et al. 2016). In Fig. 1-5b, as T decreases, more sites on the particles should become IN active thus n_m is expected to increase. It is evident that for the same n_m, Snomax activates at ~10°C warmer than pollen residues. Also, clear in Fig. 1-5b is that different fungi particles freeze between $-5°$ and $-10°C$ with IN activity that spans over four orders of magnitude in n_m. For a comparison we have plotted a subset of soil dust n_m (see next section for soil dust discussion) in Fig. 1-5b. It can also be seen that the increase in the n_m values, that is, the range where the INMs are ice active, is similar for bacteria, fungi, and lichens for $T < -5°C$, but bacteria already show an increase at a higher temperature ($\sim -3°C$) as shown in Fig. 1-5a. Pummer et al. (2015) discuss that many INMs from fungal spores and bacteria have comparable sizes, where the size then determines the temperature at which they are ice active. While the majority of bioaerosol studies focused on continental sources, there is new evidence suggesting that oceans are a significant source of biogenic INPs as shown in Figs. 1-4, 1-5a, and 1-6 (DeMott et al. 2016; Prather et al. 2013; Schill et al. 2015b; Wang et al. 2015; Wilson et al. 2015). Many of the bioaerosol studies also focused on the cells or fragments of biological particles, but it was also found that the exudates from marine microorganisms could nucleate ice under cirrus (see Fig. 1-4) and MPC (Fig. 1-5a) conditions, with the ice-active material having sizes on the order of tens of nanometers, potentially being macromolecules (Ladino et al. 2016; Wilson et al. 2015). Marine diatoms are also active INPs at $T < -38°C$ in the deposition mode over a wide range of RH_i and at $T > -35°C$, IN via immersion mode was observed (Knopf et al. 2011, see their Fig. 2).

Even though the bioaerosol emission rates are orders of magnitude smaller than dust particles (Després et al. 2012), a small fraction of some types may freeze at much higher temperatures than dust (e.g., see bacteria in Fig. 1-5a, and leaf litter or plankton data in Fig. 1-5a). This can increase their impact in the formation of ice in clouds through subsequent secondary ice processes (Field et al. 2017, chapter 7). Biological components can also be attached to other particles such as dust or sea salt enhancing the ice nucleating ability of these carriers thus increasing their atmospheric relevance (Augustin-Bauditz et al. 2016; Conen et al. 2011; Ladino et al. 2016; O'Sullivan et al. 2014, 2015; Tobo et al. 2014). Bioaerosol may contribute toward primary ice formation in field observations of atmospheric ice where more than half of all clouds are observed to contain ice at temperatures as warm as $-8°C$ (e.g., Bühl et al. 2013). However, the role of atmospherically relevant bioaerosol relative to other INPs like feldspars shown to nucleate ice at temperatures as warm as $-2°C$ (see black crosses in Fig. 1-2, Harrison et al. 2016) is yet to be determined.

e. Soil dust

Soil dust particles are emitted from grazed and agricultural lands and are believed to contribute up to 25% of the global dust emissions and have been shown to nucleate ice with an effectiveness (see Fig. 1-6) comparable to that of some bioaerosol and feldspar samples (as discussed in sections 3d and 3a). Onset temperatures as high as $-6°C$ have been found corresponding to INP concentrations of $0.01\,L^{-1}$ (Garcia et al. 2012), 0.01 (active) sites μg^{-1} of soil (O'Sullivan et al. 2014), 0.5–1 sites μg^{-1} of soil (Conen et al. 2011; Hill et al. 2016), and 0.1–1000 sites μg^{-1} of mycelium (Fröhlich-Nowoisky et al. 2015), higher than that of natural dust or clay particles where similar onsets ($0.01\,L^{-1}$) are only found to occur between $-12°$ and $-25°C$, respectively (Murray et al. 2012). The high ice nucleating ability of soil dusts is attributed to internal mixing with organic matter (biogenic components) present in the particles (O'Sullivan et al. 2014; Tobo et al. 2014). A clear indication of the important role of proteinacious organic components in the soil dust is the reduction of their ice nucleating ability after heat treatment at 90°–100°C (e.g., Garcia et al. 2012; Hill et al. 2016; O'Sullivan et al. 2014). To remove thermally stable organic carbonaceous components, hydrogen peroxide digestion is applied to soil dust particles, which also results in a reduction in their IN activity by one to two orders of magnitude in n_s at $T > -35°C$ as shown by the black, wine-colored, and gray-scaled identical symbols in Fig. 1-6 (O'Sullivan et al. 2014; Tobo et al. 2014). For $T < -15°C$, O'Sullivan et al. (2014) found that the mineral components in the soil dust become more important than the organics, which are key for IN at higher temperatures. Tobo et al. (2014) showed that minerals were more important for IN only at lower temperatures, $T < -33°C$. Ice-active bacteria from agricultural soil were not found while sampling air above the agricultural soils, suggesting that local vegetative sources did not influence the air above it, except during combine harvesting, when a significant enhancement of the

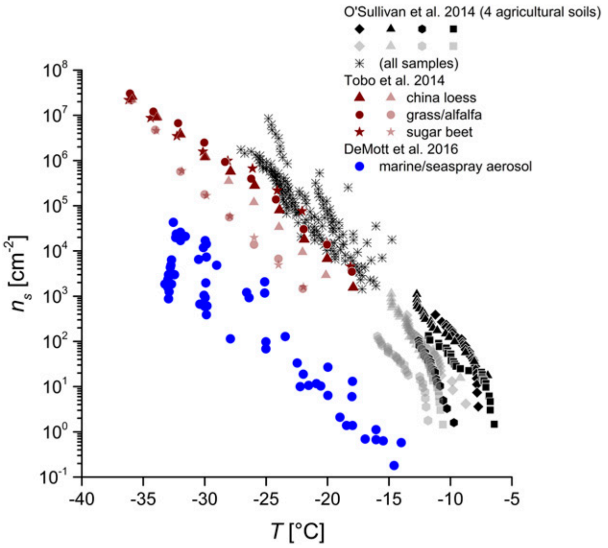

Fig. 1-6. Ice nucleation active site densities n_s as a function of temperature for H_2O_2 (hydrogen peroxide) treated (lighter-shaded symbols) and untreated (dark symbols) agricultural soil dusts in comparison to the n_s of marine aerosol. Differences between various black symbols are for organic content (OC). High OC (12.7 wt%) soil from a field not recently ploughed (black diamonds) and low OC (2.1–2.9 wt%) from field that had been recently ploughed (other black symbols).

airborne atmospheric INP population was observed (Garcia et al. 2012). For a comparison, the n_s of marine aerosol particles from DeMott et al. (2016) are also shown in Fig. 1-6. Despite an ice nucleating ability at similarly warm temperatures as soil dust, the marine particles' n_s is one to two orders of magnitude lower than the reduced IN activity of the treated soil dust samples. As such, marine INP should be important in regions of the troposphere where dust particles are absent. The atmospheric relevance of soil dusts, much like that of bioaerosol, also depends on the tropospheric budget of such particles, which is not known with reasonable certainty. The ubiquity of agricultural activities and demonstrated IN ability of soil dust implies these particles can be a key catalyzer of ice in clouds on a regional scale. Specifically, the studies discussed provide indirect evidence that the IN activity of agricultural soils is imparted by organic components internally mixed with mineral dust. Do such organic components adsorb to other atmospherically relevant carriers or only to mineral dusts? Clarification as to what is truly the INP, the organic material, or the host particle is a key knowledge gap and must be bridged.

f. Biomass and fossil fuel combustion aerosol particles

Combustion processes emit large quantities of chemically complex particles to the atmosphere of both carbonaceous and noncarbonaceous organic and inorganic composition. We broadly define two particle categories from combustion process: first, particles composed of carbonaceous matter that are formed by pyrolysis of the fuel molecules (Flagan and Seinfeld 1988); second, ash particles that are derived from noncombustible constituents (primarily mineral inclusions) in the fuel and from heteroatoms (excluding carbon and hydrogen) in the organic molecular structure of the fuel. Biomass burning (BB) particle sources include ash and smoke from forest and agricultural fires, wood stoves, heating, and industrial activities. During the combustion process, particles can be lofted leading to airborne fly ash. Soot particles are black carbon particles that have organics condensed onto them or have oxidized surfaces and are the result of incomplete combustion and can also be produced from BB. A significant source of soot, however, is from incomplete combustion of fossil fuels (e.g., during transportation and industrial activities). Fossil fuels such as coal can produce both soot and ash. Soot and ash particles may play an important role in the formation of ice clouds given their high emission rates and therefore high atmospheric concentration. However, it is still unclear if these particles are important for IN, as laboratory and field observations are contradictory (Bond et al. 2013). To facilitate the discussion below, a summary of the ice nucleating results of soot and ash particles are presented in Figs. 1-7a,b. For $T > -40$°C, only a handful of studies show soot or ash particles to nucleate ice in the immersion or contact mode, as seen in Fig. 1-7b (Brooks et al. 2014; Gorbunov et al. 2001; Grawe et al. 2016; Popovicheva et al. 2008; Umo et al. 2015) and at very high RH_w (Chou et al. 2013), as seen in Fig. 1-7a. For $T < -40$°C, several studies in Fig. 1-7a show that soot and ash particles are deposition INPs (Chou et al. 2013; DeMott et al. 1999; Kanji and Abbatt 2006; Kanji et al. 2011; Koehler et al. 2009; Möhler et al. 2005). Some recent laboratory studies also indicate that soot BB particles significantly contribute (>40% by number) to total INP concentration sampled (Levin et al. 2014; McCluskey et al. 2014). In immersion mode for $-12° > T > -36$°C, ash from BB and coal combustion can exhibit a higher n_s than clays but still less than the n_s of natural dust samples (Grawe et al. 2016; Umo et al. 2015, see Fig. 1-7b). In the cases where soot and ash particles were found to act as INPs, their ice nucleating ability appears to be linked to their fuel source and mixing state (via chemical aging or coatings) thus leading to a wide variety of results ranging from onsets of ice nucleation at $RH < RH_{hom}$ to $RHw > 100\%$ (see Fig. 1-7a). From Fig. 1-7a it is apparent that most samples activate at or above the threshold for homogeneous freezing. Notable exceptions all occurring at $T \leq -40$°C are, first, the low O:C ratio calibration aerosol standard (CAST) soot

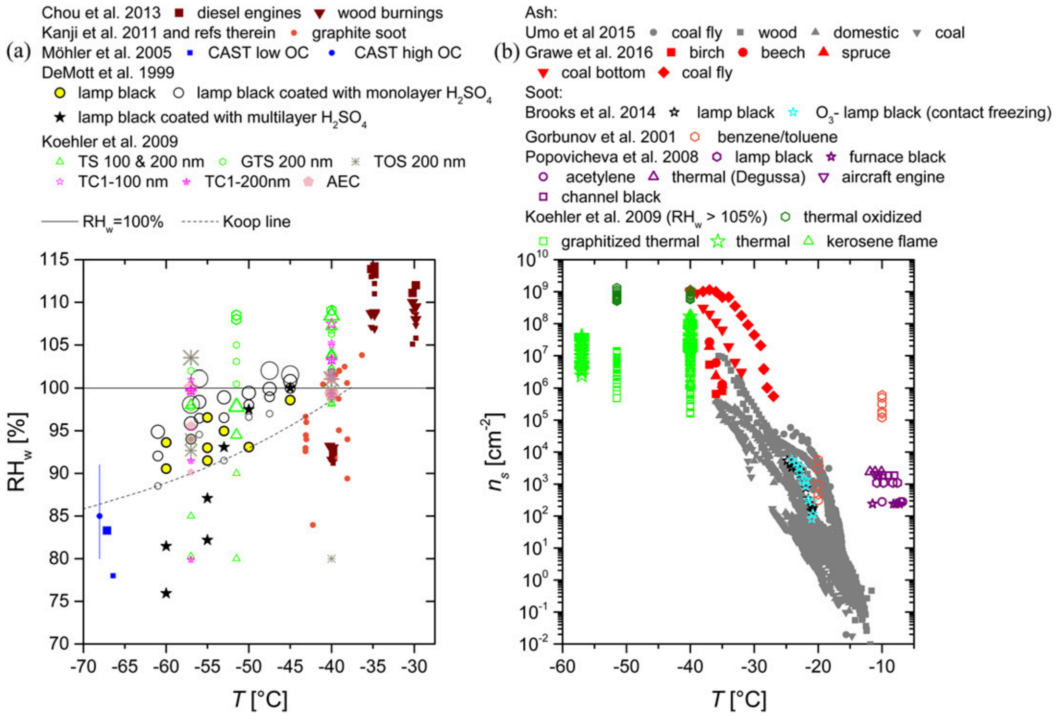

FIG. 1-7. (a) Ice nucleation onset RH*w*. (b) Ice nucleation active site densities n_s as a function of temperature for soot and ash particles. TS: thermal soot (100 and 200 nm not distinguished because of similar results), TOS: Oxidized TS, TC1: kerosene flame soot, AEC: aircraft combustor kerosene soot, GTS: graphitized TS. Smallest symbol sizes refers to first observed ice or AF ≤ 10^{-3}, and progressively larger symbols correspond to AF of 10^{-2} and 10^{-1}, with the largest being AF = 1. Solid and dashed lines as in Fig. 1-3.

compared to high O:C (blue data, Fig. 1-7a) suggesting the O:C fraction influences the ice nucleating activity (Möhler et al. 2005). Second is lamp black soot coated with sulfuric acid (H_2SO_4) for $T \leq -55°C$ compared to uncoated (or monolayer coated) particles (black circles and stars, Fig. 1-7), suggesting that the degree of internal mixing with sulfate changes the IN activity (DeMott et al. 1999). Third are diesel engine and wood-burning soot, forming ice at −40°C but above this temperature requiring unrealistically high RH (wine-colored data points, Fig. 1-7a) (Chou et al. 2013). Fourth is thermal soot (TS; Fig. 1-7a) compared to graphitized thermal soot (GTS, which is TS heated to 3000°C, Fig. 1-7a), which requires water saturation conditions at, for example, $T \sim -55°C$ (small green triangles compared to small green hexagons, Fig. 1-7a), suggesting that any internally mixed non-elemental carbon components of TS influence the IN ability (Koehler et al. 2009). Last, other data points approximately appearing at RH_{hom} threshold, for example, the graphite spark generator and kerosene soot data (orange circles and pink stars, Fig. 1-7a), vary because of plotting different AFs or particle sizes, and we refer the reader to the respective studies for a detailed discussion beyond the scope of this chapter (Kanji et al. 2011; Koehler et al. 2009).

In airborne field observations of chemical composition of ice crystal residuals in the cirrus regime, soot and ash particles have not been consistently found (Cziczo et al. 2013). From field observations in the free troposphere, DeMott et al. (2003a) found fly ash in residuals of ice activated at cirrus temperatures. Burning of biomass fuels itself releases particles with IN activity of varied efficiency (AF $< 10^{-4}$ to 10^{-2}) as reported for condensation/immersion freezing at −30°C (Petters et al. 2009). Assessing the impacts of combustion ashes as INPs on a global scale can be challenging because of the limited knowledge of its abundance (Umo et al. 2015), and local impacts may be exacerbated in the absence of more effective INPs such as dust from long-range transport (McCluskey et al. 2014). Airborne INP measurements by Prenni et al. (2009a) in the vicinity of the North Slope of Alaska report average concentrations of 1 L^{-1} at −18°C (RH_w = 102%–104%), with temporal fluctuations of up to 60 L^{-1}. Trajectory analysis suggested that the higher fluctuation was associated with volcanic ash plumes and above average concentrations of ∼10 L^{-1} were observed when BB particles from long-range transport influenced the measurements. The study of Boose et al. (2016b) showed that long-range transported BB aerosol particles arriving at Izaña in Tenerife, Spain, in the summer of 2014 resulted in INP concentrations much lower ($<3\,\mathrm{L}^{-1}$ at $-33°\mathrm{C}$, $\mathrm{RH}_w = 105\%$) than the campaign average of $23\,\mathrm{L}^{-1}$. Contributions from specific studies on how the morphology and composition of BB and fossil fuel combustion particles relate to ice nucleation, especially in the cold regime ($T < -38°\mathrm{C}$) are desirable to understand the IN mechanism(s) of these particles.

g. *Volcanic ash particles*

Volcanic ash particles are emitted into the atmosphere at a rate of ~13 Tg yr^{-1}; however, it can be higher if explosive eruptions take place (Dentener et al. 2006). Durant et al. (2008) suggested that single or multiple fine-ash volcanic particles immersed in liquid droplets will act as INPs at temperatures ranging from −13° to −23°C, similar to the immersion freezing results of Fornea et al. (2009), Hoyle et al. (2011), and Steinke et al. (2011). However, Fornea et al. (2009) observed that ash particles active in immersion mode were also active INPs for contact freezing at higher temperatures (~−8°C). More recently, Zolles et al. (2015) and Gibbs et al. (2015) found a T_{50} of volcanic ash particles below −28°C in immersion mode. Additionally, Gibbs et al. (2015) found that the T_{50} of volcanic ash particles scales with the available ash surface area per drop similar to that of dust. Hoyle et al. (2011) and Steinke et al. (2011) observed that volcanic ash particles from the Eyjafjallajökull were only active via deposition nucleation at $T < -38°\mathrm{C}$. The effective ice nucleating ability of volcanic ash particles via deposition nucleation was recently confirmed by Schill et al. (2015a), who found that volcanic ash particles from different volcanoes needed a RH_i of just 110% to nucleate ice for $T < -38°\mathrm{C}$. The IN ability of the ash particles via immersion freezing was close to homogeneous freezing conditions except for the ash sample that contained quartz and also had the highest specific surface area (Schill et al. 2015a). Field observations have also shown that volcanic ash particles can catalyze the formation of ice given that the INP concentrations were significantly enhanced when a volcanic ash plume passed through the sampling location (Bingemer et al. 2012; Prenni et al. 2009a). The IN results from volcanic ash particles suggest that these would be important INPs at colder temperatures and be of importance in the absence of other more effective INPs like mineral dust.

h. *Crystalline salts*

Dissolved salts can be directly emitted into the atmosphere by the oceans and crystallize by processes such as efflorescence, or they can form by gas-to-particle conversion of different gases from marine environments, cattle farming, and industry. Soluble salt particles (e.g., NaCl, NaI, KI, KCl) of large diameters (>25 μm) have been found to induce contact freezing at temperatures as warm as −7°C (Niehaus and Cantrell 2015). Several studies have also shown that supermicron (Abbatt et al. 2006; Baustian et al. 2010; Shilling et al. 2006) and submicron (Abbatt et al. 2006; Ladino et al. 2014) $(\mathrm{NH_4})_2\mathrm{SO_4}$ particles are able to nucleate ice heterogeneously (see Fig. 1-8). This is in contrast to the results from Chen et al. (2000) who found that submicron $(\mathrm{NH_4})_2\mathrm{SO_4}$ particles do not act as INPs but freeze homogeneously. Schill et al. (2014) also found that adding equal concentration of $(\mathrm{NH_4})_2\mathrm{SO_4}$ and organics to a SOA proxy resulted in immersion freezing much below water saturation and $\mathrm{RH_{hom}}$ (black squares Fig. 1-8). They found that $(\mathrm{NH_4})_2\mathrm{SO_4}$ allowed for water uptake resulting in immersion freezing with the SOA proxy in the core as the INP. The contrasting results can arise from differences in particle-generation methods, composition, and size of the sulfate particles used for IN experiments. Sea salt was detected in around 25% of the analyzed ice residuals collected in cirrus clouds for flights conducted over oceans where the dominant mechanism was inferred to be heterogeneous IN (Cziczo et al. 2013). NaCl has been recognized as a good CCN; however, it was rarely considered as an INP. Additionally, laboratory studies (see Fig. 1-8) of micron sized NaCl particles in both the hydrated and anhydrous form (green stars, Fig. 1-8) were reported to show deposition IN at $T < -35°\mathrm{C}$ at RH_i of ~100% and ~110%, respectively (Wise et al. 2012) and for submicron NaCl particles at slightly higher RH_i at $T < -40°\mathrm{C}$ shown by green triangles and squares in Fig. 1-8 (Ladino et al. 2016; Wagner and Möhler 2013). Similarly, proxy sea salt aerosol particles generated from commercially available Instant Ocean[2] salt material were found to nucleate ice heterogeneously for $T < -50°\mathrm{C}$ shown by the open cyan data points in Fig. 1-8 (Ladino et al. 2016; Schill and Tolbert 2014), but above this temperature ice formation was only observed at $\mathrm{RH_{hom}}$ (Ladino et al. 2016). Although crystalline salts have been found to nucleate ice under cirrus conditions, it is unlikely that those particles reach high altitudes without interacting with other atmospheric components such as organics. An example of salts mixed with organics is plotted in Fig. 1-8 where sucrose is mixed into the Instant Ocean salt yielding similar ice nucleating onsets to that of the unmixed particles. How the ice nucleating ability of salts is affected when mixed with organics is still unclear (Baustian et al. 2010; Baustian et al. 2013; Ladino et al.

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[2] Instant Ocean is a registered trademark.

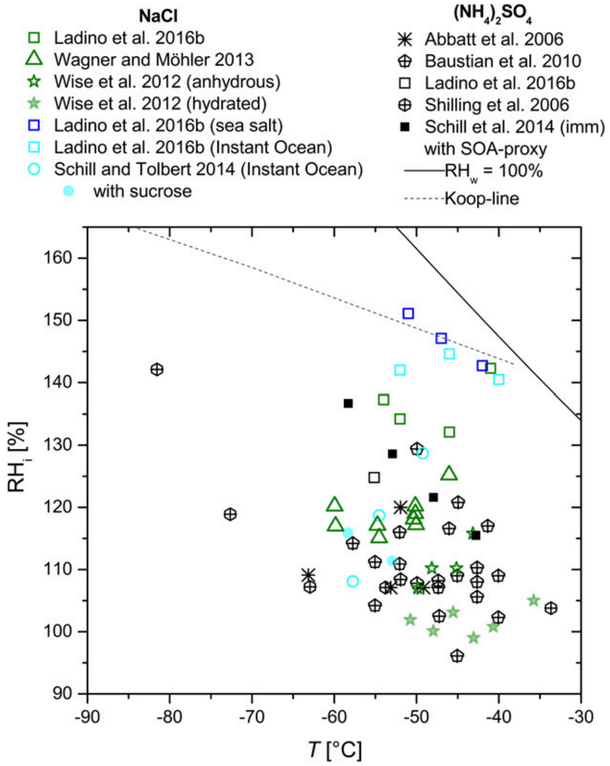

FIG. 1-8. Ice nucleation onset RH_i as a function of temperature for crystalline salt samples. Smallest symbol sizes refer to first observed ice onset or AF = 10^{-4} (Ladino et al. 2016). Larger symbol sizes are for AF = 10^{-2} (Wagner and Möhler 2013). SOA proxy refers to an equal mixture of methylamine and methylglyoxal. imm: immersion mode. Solid and dashed lines as in Fig. 1-3.

2014; Schill and Tolbert 2014; Shilling et al. 2006), but studies conducted with multicomponent laboratory generated particles of salts and organics such as sucrose, raffinose, $(NH_4)_2SO_4$, and sea salt have not shown significant differences compared to the single-component particles within the spread of RH_i observed (see purple data points in Fig. 1-3). An exception to this is the work of Schill et al. (2014), discussed in section 3c and shown in Fig. 1-3, which showed adding $(NH_4)_2SO_4$ to organics lowered the onset RH_i for IN via immersion mode. The ability of the ice nucleating process of multicomponent organic/inorganic particles is very probably and closely linked to the phase and morphology such as core-shell models resulting from liquid–liquid phase separation or water uptake onto highly viscous glassy organic cores (Lienhard et al. 2015). The spread in ice nucleating ability of salts, salt-organic mixtures, and observations of salts in ice residual compositions suggest systematic studies that probe model particle systems are needed. This should aid in understanding how the phase and chemical composition of model particles will dictate the temperature range and mechanism of heterogeneous freezing where such particles will be relevant for ice nucleation.

4. Chemically and physically modified INPs

Aerosol particles can be modified chemically and physically after being released into the atmosphere through a variety of processes occurring in the troposphere. Such processes can include physical modification via phase changes (efflorescence/deliquescence, cloud droplet/ice activation) arising from changes in temperature and humidity, or chemical modification by reaction with trace species or both.

Figure 1-9 shows an overview of potential pathways for processing of aerosol particles. For trajectories where cloud drops evaporate, the resulting droplet residual released can have modified physical properties. Such residuals could have different cloud-forming potential in a subsequent cloud cycle compared to freshly emitted particles. At higher altitudes where ice particles form, sublimation or evaporation upon melting can occur in a dissipating nonprecipitating cloud thus releasing a residual with modified IN properties (Adler et al. 2014) as shown in Fig. 1-9.

Aerosol particles can undergo chemical reactions at their surface with trace gases (O_3, NH_3, SO_2, NO_x) or inorganic components such as acids, nitrates, and sulfates or act as condensation sinks for SOA or other viscous organics forming glassy coatings. The need for representing effects of aerosol particle processing inside ice crystals for heterogeneous IN parameterizations has been reported (Spichtinger and Cziczo 2010). The effects on IN of such modified and processed particles are discussed in the following sections.

a. *Microphysical processing (preactivation via cooling and droplet or ice formation)*

Enhanced ice nucleating ability (or increased ice nucleation rate) of particles subjected to a previous IN event or droplet formation has been reported for clay particles (montmorillonite and kaolinite) provided that subzero temperatures are maintained between subsequent ice formation cycles (Pruppacher and Klett 1997). Knopf and Koop (2006) used ATD particles to show that such so-called ice preactivation is relevant for dust if the condition of subzero temperatures between cycles is maintained yielding a 10%–30% lower onset RH_i. In a cloud chamber study, Möhler et al. (2006) reported ice preactivation does not result in enhanced ice formation with ATD, while Wagner et al. (2016) reported the opposite for dust such as porous illite, diatomaceous earth, and zeolite particles. For preactivation effects to prevail, microscopic ice must survive between the first ice nucleation and subsequent ice

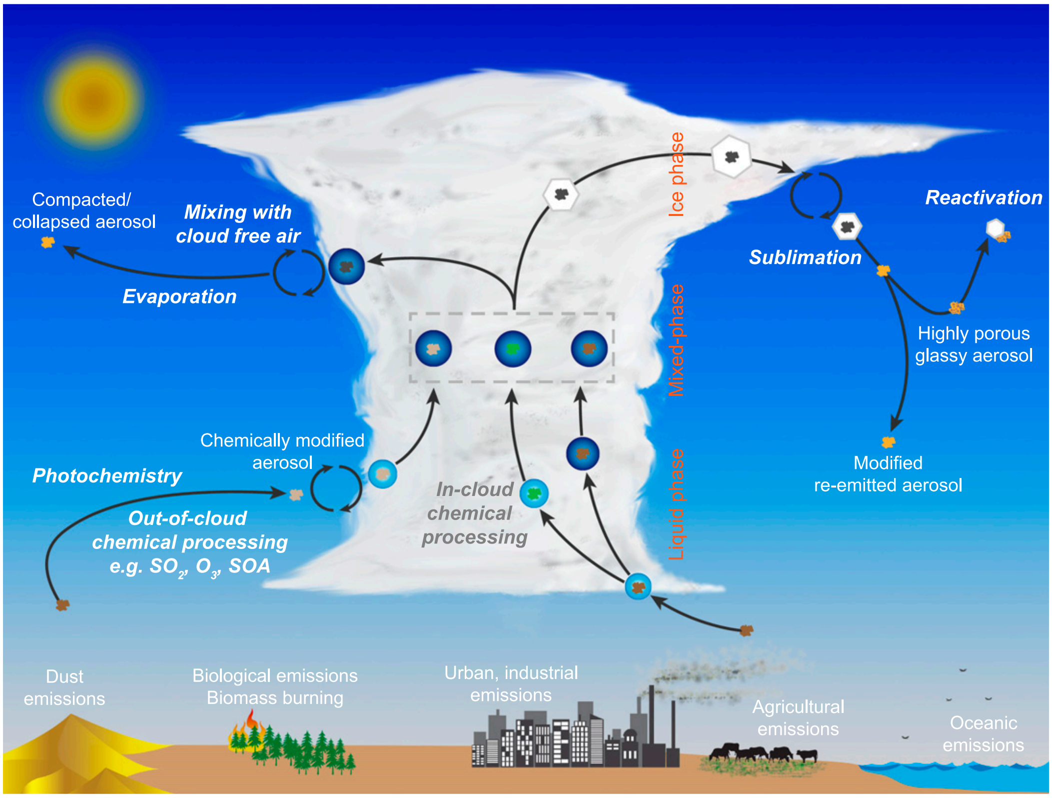

FIG. 1-9. Possible pathways of atmospheric processing and aging of aerosol discussed in this chapter (see section 4). The gray dotted box shows cloud droplets that could form via different aging pathways that can lead to modification of the aerosol. Different aerosol particle colors are to indicate that they have been modified compared to their emitted state. Bold lettering indicates processes and normal lettering, the presumed state of the aerosol resulting from indicated processes.

formation cycles. If small pores or cavities are present in the INPs so that ice would survive in the pores between ice formation cycles when $RH_i < 100\%$ because of the inverse Kelvin effect (Marcolli 2014), subsequent macroscopic ice formation would then be a growth process rather than a nucleation process and can be expected to occur upon ice supersaturation, that is, at lower RH_i than the nucleation process. This could explain the different preactivation outcome for the highly porous particles in the Wagner et al. (2016) study compared to the less porous ATD particles studied in Möhler et al. (2006). However, if RH_i falls below ~5% between the subsequent IN cycles, the preactivation effects are hindered, as was observed for ATD in Knopf and Koop (2006) and could explain why the two studies above observed different outcomes for ATD. Droplet freezing experiments (Bigg 1953; Vali 1971) with soil dust suspensions have also been used via freeze–thaw cycles and found that in ~15% of the refreeze cycles the freezing temperature changed by ±5°C, significantly more than expected from random fluctuations (Vali 2008). Vali (2008) provides speculative reasons for the observed increase in freezing temperature that include but are not limited to retention of molecular clusters for ice embryo growth on the INP sites or movement of the INP from the droplet interior to the surface at the air–water interface (Durant and Shaw 2005; Shaw et al. 2005). Reasons for the decrease in observed freezing temperatures could include the partial destruction of active sites or retention of nonoptimally configured molecular clusters for ice embryo growth (Vali 2008). However, what specific changes result in different refreeze temperatures is unknown (Vali 2014). Different experimental approaches can also influence observations and have been already considered in the discussion of respective studies above. For example, in cloud chambers settling of large particles between cloud cycles can influence results of secondary and tertiary cloud cycles. In cold stage techniques, possible substrate effects or the use of very large particles can influence ice onsets. In the case of droplet freezing experiments, imprinting the ice configuration, etching of the substrate used and contamination have been cited as possible reasons for observed differences in freezing temperature (Vali 2008). The atmospheric relevance of preactivation and refreezing for the

IN of dust particles is still unknown and could benefit from newer studies that investigate the influence of the aerosol particle morphology on the observed mechanism.

Another preactivation mechanism arises from solid or insoluble particles forming ice from short adiabatic expansion caused by airflow across the wings of aircrafts in cruise at subsonic flight levels (Kärcher et al. 2009). Not much is known about preactivation at cirrus conditions. For example, it is not known if atmospheric soot particles show preactivation effects (Kärcher et al. 2007). It is possible that evaporating contrails provide a low-temperature source of effective INPs contributing with some significance to the background concentration of effective INPs already affecting naturally occurring cirrus. This can occur upon evaporation of short-lived aircraft contrails, releasing new ice-forming soot nuclei (Kärcher et al. 2007; Suzanne et al. 2003). Retention of ice in the cavities of residual soot cores after evaporation could serve as germs for repeated growth of ice crystals into cirrus cloud particles in supersaturated air. The fractal-like morphology of soot particles may allow for the occurrence of water-filled micropores even at subsaturated conditions because of the negative curvature effect (Suzanne et al. 2003). Such processing effects are not constrained and have been rated with high priority for understanding impact of soot particles on cirrus clouds (Kärcher et al. 2007).

Organic and multicomponent mixtures are particularly susceptible to cloud processing showing enhanced heterogeneous ice formation after a cloud processing cycle. Dicarboxylic acid mixtures with $(NH_4)_2SO_4$ freeze at temperatures as warm as $-10°C$ by deposition nucleation and immersion freezing only after a cycle of homogeneous freezing at $-38°C$ provided that the temperature of the particles is maintained below the glassy transition temperature of the particles between freezing cycles (Wagner et al. 2012, 2014). Precooling and subsequent enhanced deposition nucleation possibly resulting from a change in particle viscosity was also observed for the water-soluble fraction of α-pinene SOA from flow tube and smog chamber studies (Ladino et al. 2014). Vitrification of the particles by freeze-drying in the ice phase can change particle size, for example, from 250 to 400 nm (Adler et al. 2013) and condition particles for subsequent ice formation by trapping ice embryos in the pores or capillaries of the resulting amorphous particles (Marcolli 2014). On the other hand poorer ice nucleating abilities have been shown for oxalic acid at $-29°C$ when cloud droplet activation occurs followed by evaporation and subsequent IN (Wagner et al. 2010). The water-soluble fraction of α-pinene SOA showed similar IN activity compared to freshly produced SOA particles (Ladino et al. 2014), suggesting cloud droplet activation would have no effect on the IN activity of resulting SOA droplet residuals. Identifying which particle properties give rise to enhanced cloud-forming potential after a preactivation cycle is necessary to understand how cloud processing and ice nucleating ability of aerosol particles are related.

b. *Chemical processing and internal mixing of aerosol (laboratory studies)*

Treatment or coating of dust with HNO_3 has shown that in the deposition mode, particles such as ATD, kaolinite, illite, and K-feldspar have suppressed IN activity. However, in condensation mode, ice formation was unaffected (Kulkarni et al. 2015b; Sihvonen et al. 2014; Sullivan et al. 2010a). This behavior is explained by physisorption of HNO_3 onto the dust particles, concealing active sites in the water subsaturated regime, which are then reexposed in the condensation mode when the HNO_3 coating dissolves into the water layer. H_2SO_4-coated ATD, K, and Na/Ca feldspar, kaolinite, illite, motmorillonite, aluminosilicates, and quartz all showed suppressed IN activity in the deposition mode for $T > -60°C$ and in immersion mode for $T > -36°C$ (Archuleta et al. 2005; Cziczo et al. 2009a; Sihvonen et al. 2014; Wex et al. 2014). A number of reasons have been proposed for this suppressed effect in deposition mode. These include the formation of a liquid layer caused by water uptake at $RH_w < 100\%$ forming a soluble sulfate coating resulting in a delayed onset of ice nucleation either due to freezing point depression or inhibiting the potential of vapor molecules to form ice clusters at lower RH_i as a result of the existence of a liquid layer (Archuleta et al. 2005). Another reason proposed was the formation of a soluble $Al_2(SO_4)_3$ product on the kaolinite surface resulting in changing the surface of the kaolinite itself (Sihvonen et al. 2014). Thicker coatings were found to be necessary to inhibit ice nucleating activity at water subsaturated conditions (Cziczo et al. 2009a). In particular, coatings of H_2SO_4 with thicknesses of a few nanometers were required to observe a decrease in IN activity in the immersion and deposition mode (Niedermeier et al. 2011a; Sullivan et al. 2010b; Wex et al. 2014). Reduction in ice nucleating ability of the sulfate-coated particles in immersion mode is likely due to surface modification of the particles as was observed with aerosol mass spectrometry (Reitz et al. 2011) that results in destroying ice-active sites that otherwise exist on the untreated dust particles. Compared to montmorillonite and illite, feldspar showed the largest decrease in IN activity when coated with H_2SO_4 in the immersion mode (Kulkarni et al. 2014). H_2SO_4 coatings reduced the IN efficiency of kaolinite particles partially composed of feldspar in the immersion mode but did not have an influence on kaolinite particles containing no feldspar; that is, H_2SO_4 reacts with the feldspar, thereby destroying its superior IN ability (Augustin-Bauditz et al. 2014; Wex et al. 2014).

Other treatments, such as montmorillonite exposed to NH_3 (Salam et al. 2007) and kaolinite exposed to O_3 (Kanji et al. 2013), have shown an enhancement of AF and F_{ice} for $T > -36°C$ in both deposition and immersion–condensation modes. In the respective studies, the enhanced ice nucleating effect was attributed to an increased hydrophilic nature of the particle surface due to the treatments performed. Treatment of dust particles with organics such as hydrocarbon functionalized silica (Kanji et al. 2008), α-pinene SOA-coated illite (Möhler et al. 2008) or 0.2–5 nm-thick coatings of levoglucosan and succinic acid (Wex et al. 2014) all reduce IN efficiency in the deposition mode, but for the latter case the immersion mode was unaffected. Authors reported for the suppressed IN activity, treatment or coating of the particles blocked the interaction of water molecules with active sites that would otherwise promote IN on the untreated particles.

Propane soot particles have also been aged with O_3 or oleic acid (Friedman et al. 2011) and did not show enhancement in IN activity compared to untreated soot. Similarly, IN in the deposition and condensation mode of soot particles from a diesel engine and wood burning were unaffected after photochemical aging (with oxidized volatile organic carbons) in a smog chamber compared to unaged particles of the same type (Chou et al. 2013). The response of soot particles to chemical treatments would suggest that the aging processes applied were not important to predict the ice nucleating activity or did not modify the soot particle surface enough to promote or further inhibit IN within the sensitivities of current measurement techniques.

The response of different particles and aging techniques emphasizes the unknowns with regard to the ice nucleating activity of chemically aged particles. The idealized systems of internally mixed particles summarized in this section are useful but also pose a challenge to directly relate to atmospheric INP properties where the degree of internal and external mixing is not always known. The usefulness of such experiments however, arises from understanding if the degree of IN variability from internally mixed (chemically aged) particles is significant compared to the natural variability observed in INP properties in the atmosphere at locations experiencing different levels of aged atmospheric aerosol (see Fig. 1-10 and section 5).

c. *Atmospheric processing in field measurements of INPs*

Airborne or high-altitude field sampling of INPs likely investigate processed aerosol particles particularly if they have been subjected to long-range transport prior to arriving at the sampling site. A combination of chemical aging and cloud formation could result in internally mixed particles or cooling preactivation. Determining how long-range transport influences the IN ability of such particles would require ice nucleation, chemical, and physical properties at an emission source to be compared to those sampled at a site experiencing particles from the same source after long-range atmospheric transport, which in its own right is challenging to accomplish for field measurements. DeMott et al. (2003a) examined the chemical mixing state of INPs at Storm Peak, Colorado, a site experiencing direct exposure to the free troposphere, and found up to 25% of dust/fly ash particles contained sulfates and organics implying internally mixed particles, which indicates some type of aging during atmospheric transport. For the same location, Richardson et al. (2007) reported that most dust related INPs were not coated with measurable amounts of soluble material; however, INP concentrations were lower during episodes of pollution when combustion particles coated with soluble material were sampled.

Two other locations where field measurements of INPs have been conducted are Izaña and Jungfraujoch (JFJ; Boose et al. 2016a, b; Chou et al. 2011; Conen et al. 2015). Both sites are influenced by Saharan dust (SD) particles; however, Izaña is close to the emission source, whereas SD only reaches JFJ after long-range transport. Conen et al. (2015) found that during SD events, immersion freezing INP concentrations at −8°C at JFJ were higher than at Izaña, implying long-range transport of dust and mixing with air masses containing particles of other origins (e.g., vegetated land) or being subjected to microphysical cloud processing may have increased the ice nucleating activity of the particles arriving at JFJ. Boose et al. (2016b) found a positive correlation of INP with mass of $(NH_4)_2SO_4$ at Izaña while sampling air masses that were influenced with dust from the Sahara suggesting that internal mixing with ammonium sulfate increased INP concentrations at this location. To test the potential effect of microphysical (cloud) processing, a comparison of INP concentrations sampled during in-cloud versus out-of-cloud periods was done at JFJ (Boose et al. 2016a). A small difference in INP concentration was found with $n_{s(\text{in-cloud})} > n_{s(\text{out-of-cloud})}$, suggesting that at JFJ cloud processing only played a minor role in the ice nucleating activity of the sampled particles (Boose et al. 2016a).

Studies such as those described above provide a good starting point for understanding cloud processing effects on INP concentrations but there are caveats to consider. First, it is impossible to conclusively state that an observed increase (or decrease) in n_s is due to particles having been previously activated as drops or as ice crystals from the in-cloud periods since an ice-selective inlet was not used.

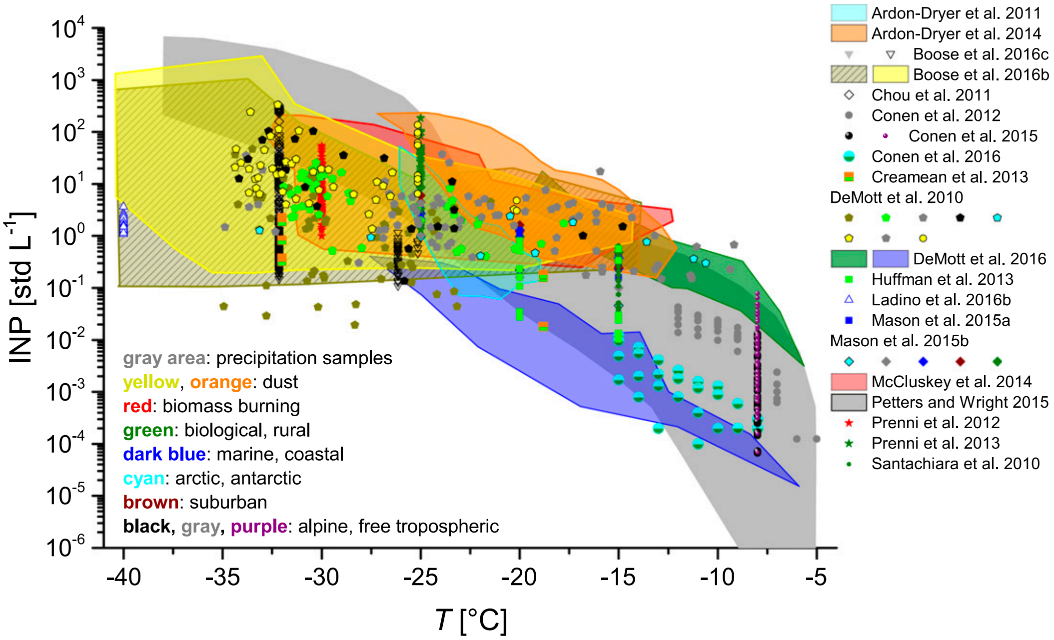

FIG. 1-10. Summary of INP concentrations taken from studies of field measurements conducted globally. Symbol colors correspond to the font color that give information on airmass type or sampling location. Dual-colored symbols indicate INP concentrations were influenced by two classes of particles or air masses. Symbol sizes in this plot are only different to avoid masking of data. Shaded areas are enclosures of data from the indicated studies and have been presented to avoid masking of individual data points. For studies where INP concentrations were not reported at standard conditions (1013 mbar and 0°C), we have derived them herein. The Conen et al. (2012) data have been pressure corrected for standard conditions. Antarctic data from Ardon-Dryer et al. (2011) are unspecified for standard conditions. Hashed area and open symbols are INP concentrations for $RH_w < 100\%$; all other symbols for $RH_w \geq 100\%$ or droplet freezing. See the legend for data from Ardon-Dreyer and Levin (2014), Conen et al. (2016), Prenni et al. (2012), and Santachiara et al. (2010).

Second, warming and drying of particles is a requirement for the operation of many INP sampling methods that can additionally induce morphological changes (e.g., vitrification) leading to variable IN abilities of ambient particles. Warming particles can also reverse the preactivation (or memory effects) if subzero temperatures are not maintained (Pruppacher and Klett 1997) making it challenging to study preactivation effects on the ice nucleating ability of ambient particles using current sampling methods. Designing an experimental system that can sample particles and evaporate (sublimate) associated macroscopic water (ice) without warming the particles to $T > 0°C$ would be necessary to understand the effects of preactivation on ice nucleation. Such experiments are challenging to undertake in field campaigns or on airborne platforms; nonetheless, validation that preactivation is occurring in the atmosphere is necessary and could represent a major advance in the field.

5. Atmospheric relevance of the different types of INPs

To demonstrate that the different broadly defined categories of INPs discussed in section 3 are also found in the atmosphere, although likely as internally mixed particles, we summarize field data of INP concentrations as a function of T in Fig. 1-10 taken from the literature. Where possible we have stated the broader compositional class, type of air masses being sampled, or locations of the sampling site to help identify the most likely particle population contributing to the observed INP concentrations. A general observation that is to be expected from CNT and has already been made early on (aufm Kampe and Weickmann 1951) is roughly an exponential increase in INP concentrations with decreasing temperature. DeMott et al. (2016) report an increase in INP concentration by a factor of 10 for a temperature decrease of 5°C for sampling of marine air, which is similar to observations by Petters and Wright (2015) for global precipitation samples (see Fig. 1-10). However, at any one temperature, the spread in observed INP concentrations is several orders of magnitude irrespective of airmass or particle compositions being sampled and a parameterization based on a simple exponential fit does not describe the observations. To overcome this, DeMott et al. (2010) developed a parameterization from 14 years of INP and aerosol particle field measurements conducted mostly over continental regions (United States, Canada, the Amazon), but also sampling aerosol over the Arctic and dust and continental pollution over the Pacific basin [see data in Fig. 1-10 and discussion in section 7a(3) for more details on parameterization].

It is inferred from discussions above and from the measurements shown in Fig. 1-10 that IN activity at high temperatures ($T > -10°C$, possibly even above $-20°C$) is typically based on continental biological ice nucleators of plant and soil with biological components (Garcia et al. 2012; Pummer et al. 2015) but can also be from marine sources shown in DeMott et al. (2016) and suggested in Wilson et al. (2015) by analysis of ocean microlayer samples and using a climate model to globally extrapolate results. However, the contribution from continental sources can be up to three orders of magnitude higher at $T > -20°C$ (DeMott et al. 2016), suggesting marine sources could be important in the absence of other more ice nucleating active aerosol species. The contributions to INP populations at lower temperatures ($T < -15°C$) are expected to be mostly due to feldspar- and quartz-containing dust (Atkinson et al. 2013; Boose et al. 2016c), with soil dusts of agricultural origin making a nonnegligible contribution even if it is assumed that 5%–25% of total dust emissions are of agricultural origin (Tobo et al. 2014). While feldspar is more ice active than ash, soluble and glassy particles, and soot, it is important to note that for all INP types, their actual contribution to atmospheric ice formation is always an interplay between their availability and their IN ability at any one temperature. For example, Wilson et al. (2015) estimated global atmospheric INP concentrations over oceans based only on the presence of INPs from marine biota and K-feldspar particles. The modeled INP concentrations in the Southern Hemisphere were comparable to values from former surface-based measurements (Bigg 1973; Rosinski et al. 1987), pointing toward an only small role for dust from deserts in the respective regions. In general, INP number concentrations at $-20°C$ and 850 mbar were found to largely originate from marine biogenic sources in the Southern Ocean, the North Atlantic, and the North Pacific, while INPs from desert dusts were dominant elsewhere. However, calculations by Wilson et al. (2015) also clearly show that overall INP concentrations depend on location, season, temperature (i.e., heights) of cloud formation, and the availability of different types of INPs. A few ice-active biological INMs, if present, might nucleate ice at a higher temperature before equally present dust particles become ice active, influencing the overall cloud development and thus the contribution of different INP types to the IN process.

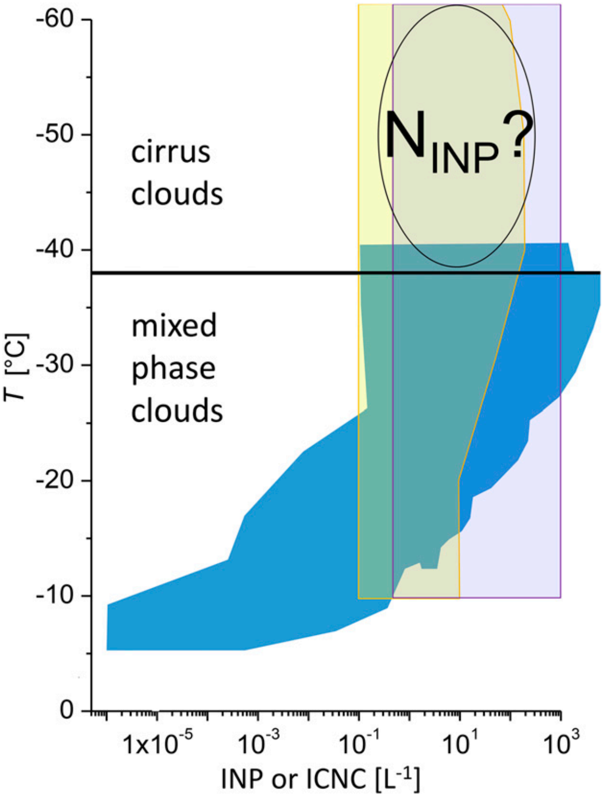

FIG. 1-11. Enclosure (blue-filled shading) of atmospheric INP concentration range (from Fig. 1-10) presented in context of atmospheric temperature and cloud regime. For the cirrus regime, similar numbers are not known. The light purple area indicates observed atmospheric in-cloud ice crystal number concentrations indicating that secondary ice formation can be expected to occur, increasingly so for increasing temperatures. The yellow shading represents measurements for ice crystals with $d > 50\,\mu m$ and the purple shading for ice crystals with $d < 50\,\mu m$. The range of ice crystal number concentration is derived from measurements using the New Ice Experiment–Cloud and Aerosol Particle Spectrometer (NIXE–CAPS; Krämer et al. 2016) in the Arctic, at midlatitudes, and in the tropics.

6. Challenges in understanding of INPs and their role in microphysics

a. Discrepancy between INP concentration and ice crystal number concentration

For several decades field observations have shown a discrepancy between the ice crystal number concentration (ICNC) and measured INP concentrations [see references in Cooper and Vali (1981) and Mossop (1970)] of up to four orders of magnitude at $-10°C$ (Auer et al. 1969) or modeled INP concentration of up to five orders of magnitude (Lloyd et al. 2015). In Fig. 1-11 we show an enclosed blue-filled shaded area representing the range of INP concentrations observed from field sampling taken from Fig. 1-10 juxtaposed with the

ICNC reported in recent literature. There is a tendency for the discrepancy between ICNC and INP concentrations to increase with increasing temperatures, with the difference being as high as five orders of magnitude. Under very specific conditions, a good agreement between the INP concentrations and ICNC has been observed in wave clouds (Eidhammer et al. 2010; Field et al. 2001, 2012; Twohy et al. 2010) and frontal clouds (Stith et al. 2011). One of the suggested explanations for the discrepancy was the shattering of ice particles caused by the cloud probe inlets in former measurements. However, similar discrepancies are still detected in recent observations where antishattering tips (Korolev et al. 2011) were used (Ladino et al. 2017; Lasher-Trapp et al. 2016; Lawson et al. 2015). Although the formation of ice particles via homogeneous freezing typically takes place at high altitudes, they could induce secondary ice formation at lower altitudes by sedimentation into supercooled liquid or MPCs from above. This can cause secondary ice particle production, which has been identified as a likely explanation of the high ICNCs observed in field measurements (DeMott et al. 2011; Heymsfield and Willis 2014 and references therein). It has been shown that the ''Hallett–Mossop (H–M)'' or ''rime splintering'' mechanism is highly effective at −5°C (Hallett and Mossop 1974). A more rigorous discussion on secondary ice processes and ice multiplication can be found in Field et al. (2017, chapter 7). High ICNC observed at temperatures close to 0°C likely originate from the H–M mechanism with bioaerosol or some feldspar-containing particles (Harrison et al. 2016) potentially being important given that at these high temperatures bioaerosol (Hoose and Möhler 2012) and feldspar minerals are the only aerosol particle types that have been shown to nucleate primary ice particles. In studies of aged wintertime cumulus clouds in the United Kingdom by in situ aircraft and remote sensing measurements, Crawford et al. (2012) found that in the absence of high-altitude ice particles falling to the lower cumulus levels, an INP concentration of $0.01\,\mathrm{L}^{-1}$ was the minimum required to nucleate primary ice, which then in the presence of falling drizzle drops (which form through collision and coalescence) produce ICNCs of $\sim 100\,\mathrm{L}^{-1}$ via the H–M mechanism at $T \sim -7.5°\mathrm{C}$.

b. Role of primary ice nucleation in secondary ice processes

Even though it may be possible to determine if a primary particle was formed via homogeneous freezing or heterogeneous freezing, it is very difficult to identify the source and distinguish the primary ice particles that are responsible for secondary ice production. This inhibits the quantification of the importance of INPs in the production of secondary ice. Although there are several parameterizations that correlate the aerosol particle concentration and the INP concentrations as a function of temperature or aerosol particle size, too many unknowns exist in order to predict the ICNC by either aerosol particle concentration or INP concentration (see Field et al. 2017, chapter 7). To accomplish this, it would be necessary to combine methodologies where atmospheric INP concentrations are measured in all size ranges [compared to a single method with limited INP size range detection, see Cziczo et al. (2017, chapter 8)] so as to arrive at a more representative value of total INPs to define the contribution of primary ice particles at MPC levels to secondary ice production.

c. Challenges in representing INPs that show a high variability in ice nucleation

Processes that significantly change the ability of a particle to act as an INP, are difficult to parameterize for IN without making significant assumptions. For example, preactivation that would enhance or chemical aging that would suppress the ice nucleating abilities of aerosol particles would require detailed formulations of physical relationships between aging and IN processes—which are still unknown. Chemical processing can lead to varying effects, the reasons of which are poorly explored and therefore hard to parameterize based on current laboratory results.

Whether preactivation through cloud processing is effective in the atmosphere depends on the chemical and morphological nature of ambient particles and their trajectories and history after being exposed to a preactivation process like contrail formation for example. Laboratory studies would be a viable option to address this issue (Kärcher et al. 2009). Therefore, experiments must be carefully designed to delineate between confounding influences that affect the ice nucleating process. For example, what is the cause of enhanced ice nucleating abilities arising from a coating procedure that also results in particle size increases, is it the coating effect, or the larger size of the coated particle? An observed change in ice nucleating activity between coated and uncoated particles cannot therefore be attributed solely to the coating because the increase in particle size (i.e., surface area) could also produce changes in IN activity. Similarly, if cloud processing modifies both particle morphology and chemical composition, delineating which effect and to what extent it is responsible for changes in the ice nucleating ability is necessary.

The different heterogeneous mechanisms by which ice can nucleate add to the complexity of parameterizations, as processes affecting one mechanism may not affect another (see section 4b). Furthermore, the importance of microphysical and chemical processing for contact freezing is completely unexplored in laboratory experiments compared to immersion freezing. One of the reasons is the unknown contribution of contact freezing to IN processes largely arising from challenges in quantifying collision frequencies between aerosol particles and cloud droplets at the appropriate temperature, RH_i, and particle sizes relevant for the atmosphere (Ladino Moreno et al. 2013).

7. Challenges and discrepancies in parameterizing INPs for modeling and predictability

Representation of cloud microphysical processes in climate models is challenging because fundamental microphysical details are poorly understood, for example, such as unknowns regarding primary and secondary ice formation in mixed-phase and ice clouds, and assumptions that ice particles and cloud droplets are spatially homogeneously distributed. The spatial scales of processes that modify ice nucleation occur on a smaller scale than represented in global circulation models (GCMs; Boucher et al. 2013) requiring parameterizations. Here we briefly present an overview of parameterizations currently used in models and their limitations. However, we note that in addition to climate and cloud models, INP parameterizations developed based on laboratory or field studies (see discussion below) have also been used to inform lidar retrievals of INP concentrations as done by Mamouri and Ansmann (2016).

a. Types of parameterizations developed for INP representation in models

There are two main frameworks that are used to describe INP parameterizations: a time-dependent framework that can be based on CNT or based on other empirical derivations, such as the time-dependent freezing rate model (Vali 1994; Vali and Snider 2015), and a time-independent approach based on the singular hypothesis (deterministic), which describes ice nucleating active surface sites as a function of temperature only. The idea of time being of secondary importance was already suggested in Langham and Mason (1958) and also applied in the analysis of DeMott (1990) to evaluate the IN of soot particles. The usefulness of singular versus stochastic descriptions (Vali 2014) and the demonstrations of a weak time dependence using repeated freeze–thaw cycles of precipitation samples and suspensions of clays, dusts, soot, and bacteria has been reported (Wright et al. 2013; Wright and Petters 2013).

Parameterizations that also fall into the time-independent category are developed based on fits to atmospheric INP measurements as a function of temperature and aerosol particle size distributions (e.g., DeMott et al. 2010): older empirical parameterizations based on a suite of INP measurements at various locations also related INP concentration to temperature but not to aerosol particle properties (e.g., Fletcher 1962) and, last, a parameterization that relates INP number to only supersaturation with respect to ice based on measurements from CFDCs (Meyers et al. 1992).

1) DETERMINISTIC–TIME-INDEPENDENT APPROACH

This approach assumes that the influence of stochastic fluctuations of the ice germ size does not influence the freezing temperature of a particle or droplet; that is, each aerosol particle is characterized by a freezing temperature (T_c) and freezing would occur as long as the particle temperature is below T_c. A surface density of sites active on a particle surface that can initiate IN at a given temperature, $n_s(T)$, assumes that one site gives rise to a single ice crystal. The fraction of particles that result in freezing at a given temperature, $F_{\mathrm{ice}}(T)$, can be given by (Vali 1971)

$$F_{\mathrm{ice}}(T)=\frac{N_{\mathrm{ice}}(T)}{N_{\mathrm{tot}}}=1-\exp[-n_s(T)A], \qquad (1\text{-}1)$$

where $N_{\mathrm{ice}}(T)$ is the number of frozen particles (or ice crystals) at a given temperature, and N_{tot} is the total number of particles given by $N_{\mathrm{droplets}} + N_{\mathrm{ice}}$ in cases where all particles of the given species are within droplets or ice crystals in the experiment or given sampling period. The value of N_{tot} can also be given by the total aerosol number in the experiment or sampling period when all particles are not activated to droplets and/or ice and A is the surface area of the INP. Since $n_s(T)$ can be empirically derived for a given particle type, only the aerosol particle surface area is required to predict the F_{ice}. As such it is easy to implement in models, however, it would require additional suite of instrumentation to measure aerosol particle surface areas. In addition, it requires validation that the entire surface area characterizes a specific type of INP, which may not be true for internally mixed particles. Many empirical studies have developed parameterizations based on $n_s(T)$ (Connolly et al. 2009) for immersion freezing on different types of INPs such as ATD (Niedermeier et al. 2010), desert dusts (Niemand et al. 2012), illite (Broadley et al. 2012), kaolinite (Welti et al. 2012), and feldspar by Atkinson et al. (2013), who also implemented the parameterization in a global model. In the deposition mode, the surface area dependency has been shown on desert dusts (Connolly et al. 2009), hematite (Hiranuma et al. 2014b), and ATD (Kanji and

Abbatt 2010). In particular, Vali (2014) assessed more recent data published in the literature dating back to the early 1990s to conclude that stochastic effects (time dependence) are of less importance compared to deterministic effects (temperature dependence) because of the dominance of specific active sites to promote IN. This allows meaningful use of the deterministic model, but time dependence should be accounted for in certain experiments and nucleation models under certain conditions. For example, $n_s(T)$ may work well for cases in the atmosphere where cooling rates are high ($\sim$1°–2°C min^{-1} corresponding to updraft velocities of $\sim$1.5–3 m s^{-1}) because of the high sensitivity of IN to temperature, which also explains the validity of empirically derived expressions that neglect time as a parameter (Ervens and Feingold 2013; Kanji et al. 2013). An uncertainty of $\Delta T \pm 0.2$°C results in a similar uncertainty as differences in time of a factor of 100 (Ervens and Feingold 2013). Last, time-independent deterministic parameterizations have also been developed based on laboratory and field data of dust particles acting as INPs and are discussed in more detail in section 7a(3) (DeMott et al. 2015).

2) CNT-BASED, TIME-DEPENDENT (SINGLE- AND MULTICONTACT ANGLE, STOCHASTIC)

The fraction of INPs ($F_{\rm ice}$) with surface area (A) active in a given heterogeneous ice nucleating mode at a certain temperature and saturation with respect to ice (S_i) is given by (Pruppacher and Klett 1997)

$$F_{\rm ice}(T) = 1 - \exp(J_{\rm het}A_i\Delta t), \tag{1-2}$$

$$J_{\rm het}(T, S_i, \alpha) = \mathcal{K}\exp\left[-\frac{\Delta G(T, S_i)f_{\rm het}(\alpha)}{kT}\right], \quad \text{and} \tag{1-3}$$

$$f_{\rm het}(\alpha) = \frac{(2+\cos\alpha)(1-\cos\alpha)^2}{4}, \tag{1-4}$$

where k is the Boltzmann constant and Δt (s) is the nucleation time period, typically given by the time aerosol particles are exposed to a given T (K) and S_i. The kinetic parameter $\mathcal{K}$ describes the rate at which molecules from the vapor phase are incorporated into an ice germ. However, the composition and value of $\mathcal{K}$ is debated (Thomson et al. 2015; Welti et al. 2014) but is thought to be composed of the water molecule flux to the ice germ, the packing density of water molecules adsorbed and diffusing on the ice nucleating surface, and a Zeldovitch factor that incorporates the volume of the ice germ and temperature-dependent nature of the volume of a water molecule in ice. A more detailed discussion of the constituents of $\mathcal{K}$ is beyond the scope of this chapter but has been presented elsewhere (Chen et al. 2008; Pruppacher and Klett 1997; Thomson et al. 2015; Welti et al. 2014). Based on the kinetic coefficient of homogeneous nucleation, $\mathcal{K}$ has been estimated to be on the order of 10^{24} m^{-2} s^{-1} (Fletcher 1969). Values ranging from 10^{28} to 10^{31} m^{-2} s^{-1} have been proposed (Fletcher 1959) and used (Pruppacher and Klett 1997) but confirmed to be too high by Fletcher (1969). Using deposition mode experiments on kaolinite particles, more recently Welti et al. (2014) proposed values of $\mathcal{K}$ as low as 10^{9}–10^{11} m^{-2} s^{-1} for specific experimental parameters (T, t, S_i) with a maximum value below 10^{19} m^{-2} s^{-1} for the temperature range −20° to −55°C. Similarly, Trainer et al. (2009) proposed 10^{20} m^{-2} s^{-1} for low-temperature deposition nucleation on silicon wafers. Many physical processes are considered to be rather insensitive to the value of $\mathcal{K}$ over a few orders of magnitude; however, for low temperatures this maybe a problematic assumption (Thomson et al. 2015). The change in Gibbs free energy ΔG is necessary for the formation of a critical ice cluster. The term $J_{\rm het}$ is the heterogeneous nucleation rate coefficient. The scaling factor $f_{\rm het}$ describes the reduction in the free energy barrier due to the presence of a surface. Because $f_{\rm het}$ cannot be deduced a priori, it is typically used as a fitting parameter. It can be described in various ways, including as a function of a contact angle (α) [see Eq. (1-4)], which can be described as a single-contact angle for an entire population of INPs (singular stochastic) or a distribution of contact angles for the population of INPs (α-PDF) (Marcolli et al. 2007). The single-contact-angle model does not work to predict $F_{\rm ice}$ for dust particles or particles that have heterogeneous surfaces. Multicomponent stochastic models describe a distribution of active sites on each particle that would result in freezing at a given temperature (i.e., distribution of contact angles on a single particle surface). The multicomponent approach combines important aspects of both CNT framework and deterministic approaches (e.g., Broadley et al. 2012; Niedermeier et al. 2011b), that is, active sites each have a given nucleation rate coefficient described by a contact angle (Lüönd et al. 2010; Marcolli et al. 2007; Murray et al. 2011; Murray et al. 2012; Niedermeier et al. 2014; Vali 1994; Welti et al. 2012). The α-PDF/multicomponent model best describes INP behavior of particles with heterogeneous surfaces such as dust (Lüönd et al. 2010). In general the active site or α-PDF can be a proxy for surface mineralogy. Thus, the multicomponent stochastic model would be one way to parameterize the inherent high variability in ice nucleating behavior of particles.

3) DETERMINISTIC PARAMETERIZATIONS OF OTHER TYPES

Parameterizations derived from laboratory measurements that are conducted on single particle species differ from atmospheric INP measurements used to derive parameterizations that are not constrained by a single particle type. For example, Richardson et al. (2007) present a parameterization that can predict measured ambient INP concentration based on the concentration of aerosol particles larger than 300 nm at one location implicitly assuming a single type of particle, given that size was the only particle property input required. Later, DeMott et al. (2010) updated this to a parameterization using the observed particle number concentration larger than 500 nm ($n_{a>500\mathrm{nm}}$), based on a large number of field datasets taken globally as shown in Fig. 1-10, of which a temperature-dependent fraction is assumed to act as INPs. The parameterization developed might be airmass dependent (Tobo et al. 2013), and the general validity of this approach has yet to be shown but has been implemented in lidar studies (Peng et al. 2015) and modeling studies (Tan et al. 2016) and evaluated against independent field data from different air masses (Boose et al. 2016b). Later, yet another updated immersion freezing parameterization for dust only, but also based on $n_{a>500\mathrm{nm}}$ by DeMott et al. (2015) was presented. Thus, with enough evidence, the DeMott et al. (2015) parameterization could be implemented for any system, for example, being evaluated against field data in Schrod et al. (2016). The parameterization has a number of fitting parameters including one that is suggested to account for instrumental differences but also incorporate other uncertainties (DeMott et al. 2015). These parameterizations are therefore easy to implement in models based on variables (e.g., size distribution) that can help predict INP concentrations without determining the nature of the INP (DeMott et al. 2010). Another parameterization presented based on observations from CFDC INP measurements and aerosol particle data is that of Phillips et al. (2008), who construct an IN spectrum for subzero temperatures and $\mathrm{RH}_i > 100\%$ and apply this to three particle categories: dust/metallic, soot, and organics. More recently, this empirical parameterization was updated where the organic particle category was redefined as primary biological aerosol particles that replaced insoluble organic particles, and a fourth category was introduced representing soluble organic aerosol particles (Phillips et al. 2013). The new parameterization tested well against observations from laboratory and field studies that were not used in its construction.

b. *Limitations of both types of parameterizations*

The deterministic (time independent) approach is useful because of an explicit temperature dependence but is of limited use in large-scale models that require a wider temperature range, because they have been shown to be unreliable outside the temperature range they are fitted to (Hoose and Möhler 2012). For instance, it would be challenging to find one parameterization developed based on a fit to measurements conducted from fairly modest supercooling of $\sim -5°\mathrm{C}$ to $-38°\mathrm{C}$, therefore covering the entire heterogeneous ice nucleation regime. However, this should become possible by combining INP data from online and offline IN measurement techniques thus covering the entire heterogeneous temperature regime as is done recently for marine air in DeMott et al. (2016). Furthermore, this approach assumes that the ice nucleating ability is uniform over a variety of sizes. However, if the composition changes with size, the ice nucleating ability per surface area will also change and $n_s(T)$ will not work as a good predictor in such cases.

CNT single-contact-angle parameterizations implemented in models fail to reproduce the temperature dependence of immersion freezing, the temperature and supersaturation dependence of deposition nucleation, and the overall time dependence. These models can overpredict ICNC, as do other simpler stochastic models, likely because of simpler treatments like cloud liquid water content alone being responsible for ice formation (Vali and Snider 2015) or because of the lack of constraints such as vapor depletion from initial ice nucleation of efficient INPs (Eidhammer et al. 2009). Complexity and computational costs of representing more than one contact angle (α-PDF and multicomponent) in models is high. Despite this, these are the most representative models for the freezing behavior of particles with heterogeneous composition as would be expected in the atmosphere.

c. *Other factors (model limitations) that contribute to discrepancies*

1) TYPES OF MODELS

The decision of which model to use to perform simulations to test INP parameterizations depends on the scientific questions being asked. Questions that require finescale modeling such as that of a single cloud would be better done with cloud-resolving models (CRMs). CRMs have a gridbox resolution to explicitly simulate a single cloud but can also represent cloud systems and can be run long enough to represent a few cloud cycles. Microphysics in CRMs is a subgrid process and therefore parameterizations are required. Using CRM simulations allows an assessment of INP parameterizations on, for example, the persistence of single clouds (life time effect) or ice crystal size distributions and concentrations, and INP recycling (cloud processing) and entrainment (e.g., Savre and Ekman 2015). Detailed CRMs are used to develop INP parameterizations and establish physical relationships that could then be used in global models. In CRMs, however, it is not possible to assess the impacts of implementing INP parameterizations on the radiation budget, which is crucial to climate predictions. Another limitation is that it is hard to upscale established physical relationships to larger models because of different resolutions. For example, because of large grid boxes in GCMs, there is no cloud-scale vertical velocity in them.

For an overview on the effects of INPs on the global scale, GCMs are used in the assessment of the impacts of different INPs such as $(NH_4)_2SO_4$ (Abbatt et al. 2006), lead-contaminated particles (Cziczo et al. 2009b), feldspar (Atkinson et al. 2013), and dust INPs (Kuebbeler et al. 2014) on the radiation balance. The coarser resolution in these models yields an averaging effect of INPs on cloud properties within a grid box, requiring an assessment of regional or total column averages to see an effect of INPs on cloud microphysical and radiative properties. For climate modeling purposes it is therefore not advantageous to represent molecular-level changes influencing IN, but rather effort should be applied into developing simpler parameterizations. Dynamics in global models tend to overshadow aerosol particle effects, which makes studying small-scale processes challenging as numerous sensitivity studies need to be conducted to ensure observed differences arise from introduced INP parameterizations and not from effects such as mesoscale dynamics. Having an INP parameterization based on aerosol particle number or surface area requires models with one-moment aerosol particle schemes to make assumptions about the particle number or surface area or use two-moment schemes (Hoose et al. 2010; Kuebbeler et al. 2014), for instance, with prognostic equations for mass mixing ratios and number concentrations from which particle number or surface area can be calculated. The more sophisticated the aerosol particle schemes become, the higher the computational costs, thus representing processes of replenishing particles from evaporation of cloud droplets or ice crystals (aging of aerosol particles) at cloud edge, for instance, would contribute to such high computational costs (U. Lohmann 2016, personal communication).

2) PROCESSES CONSIDERED IN MODELS

Climate models now include physically based equations for cloud ice, allowing a more realistic treatment of MPC processes and ice supersaturation. Such schemes are tested against field observations (e.g., Klein et al. 2009; Kuebbeler et al. 2014; Lohmann and Hoose 2009) or satellite observations (e.g., Kay et al. 2012) and do provide superior simulations of cloud types than previous model versions (Kay et al. 2012). However, new representations of the Wegener–Bergeron–Findeisen effect that compare the water vapor depletion rate to the condensation rate arising from high updraft velocities are not included in most standard model versions. In addition, standard model versions also suffer from the lack of accurately representing other important processes not directly linked to IN, such as effects of preexisting ice and thus availability of water vapor for heterogeneous or homogeneous IN, accurately resolving updraft velocities within a grid box, and subgrid temperature fluctuations (Kuebbeler et al. 2014), all of which are important to accurately represent the effects of heterogeneous IN processes. Last, impacts on IN properties of atmospheric chemical aging resulting in internal mixing and cloud processing of INPs are also not explicitly represented in most models (Spichtinger and Cziczo 2010), largely because observations and laboratory studies on aging have produced variable results but also because of computational costs as discussed above. Simpler sensitivity studies have been conducted where ice nucleating thresholds (T and/or RH_i) have been adjusted within models to reflect those of different compositions (less or more effective INPs), thus implicitly representing atmospheric aging processes or particle composition changes. Modeling studies also assume different mineral components of atmospheric dust to be externally mixed to investigate INP parameterizations (Atkinson et al. 2013; Hoose et al. 2008). In reality, however, atmospheric dust components are typically internally mixed. Overall, the accuracy with which aerosol particle processes are represented in models is a key because even the most sophisticated and accurate IN scheme is unworthy in a model with poor aerosol representation. Where the extra complexity in models is most beneficial is a crucial question. Is it for increased horizontal and vertical resolution, which improves the dynamics, or rather for aerosol and cloud microphysical parameterizations? That decision depends on the scientific question being investigated.

8. Summary of recommendations

In the past decade a significant number of data have been collected, resulting in a reasonable advance in understanding which aerosol species are able to nucleate ice at tropospherically relevant temperatures and saturation conditions. Furthermore, individual components of dust (e.g., oxides, feldspars, clays) have also been investigated to understand which constituents may control the ice nucleating abilities of dust particles. Similar work with bioaerosols is ongoing to identify which of their components (e.g., macromolecules) or which species of bacteria, pollen, lichen, or fungal spores are active INPs. Investigations of organic-rich marine aerosol and organic-rich soils are also garnering substantial attention as newer candidates for INPs. However, the unconstrained budgets of fertile soils (agricultural dust) and biologically rich aerosol particles pose a challenge to assess their atmospheric relevance. Studies conducted have allowed us to reinterpret conventional wisdom of what makes an active INP. However, there remain a number of unknowns, as summarized below:

- The identity of an active site that controls the IN activity of INPs remains largely unknown. Explanations include the particle surface chemistry (functional groups), ‘‘bulk’’ composition (in the case of macromolecules), the particle/surface solubility, the ions released from the particle (for immersion mode), the surface morphology, or the crystal lattice structure of an exposed site. To understand how IN scales with the size and surface area of an INP, the relative roles and identity of which of the above particle properties constitute an ice nucleating active site needs clarification. Designing studies to target this unknown is of utmost importance to improve predictability of aerosol particles as INPs.
- The uncertainty and contradictory nature of results from IN studies concerning biomass burning and fossil fuel burning particles warrants systematic approaches to characterize the composition and morphology of such particles to assess their ice nucleating ability for varying sources of fuel, temperatures, and saturations that are relevant to tropospheric ice formation.
- Varied ice nucleating abilities are reported for organic-rich particles of biological (INMs) and biogenic origin, likely because of their complex chemical composition and varying viscosities dictating the particle phase. In the troposphere, organic particles can be mixed with inorganic salts or mineral dust particles, further complicating their chemical and IN characterization. Laboratory studies in their design should be informed by outcomes of field measurements in order to develop parameterizations that realistically represent IN of organic-rich particles.
- Methods are needed to identify the distribution and partitioning of INMs and biogenic organics in atmospheric (airborne) aerosol. Information on whether biogenic organics only impact atmospheric IN as adsorbed species on airborne dust particles, or if other host particles and pathways are possible for becoming airborne, will aid in the need to better represent INMs in models.
- The interplay between morphology and chemistry of atmospheric aerosol particles, both properties that contribute to heterogeneous IN, are substantially influenced by cloud processing (preactivation and/or chemical aging). The impact of preactivated particles on IN in the cirrus and mixed-phase temperature regimes is unknown despite particles being estimated to undergo up to three cloud-forming cycles before being terminally scavenged. Understanding preactivation of ice arising from cloud processing would represent a significant leap in our understanding of IN in the atmosphere.
- Conditions under which atmospheric transport, aging, and the resulting internal mixing of aerosol particles modify the ice-forming potential of INPs are highly uncertain. Unknowns exist about the fate of such particles. While investigating idealized systems is important to understand the causes of variability in ice nucleating activity, studies should also be informed by comparing INP properties of atmospheric particles close to emission sources and contrasted to ice nucleating properties of similar particles undergoing long-range transport.
- Observations of INP concentrations in the cirrus regime are lacking. A focus on the type of mechanisms relevant (e.g., deposition nucleation) and quantification of INP concentration would lead to a more complete assessment of the relationship between ICNC and INP concentration in this cloud regime.

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REFERENCES

Abbatt, J. P. D., 2003: Interactions of atmospheric trace gases with ice surfaces: Adsorption and reaction. *Chem. Rev.*, **103**, 4783–4800, doi:10.1021/cr0206418.

——, S. Benz, D. J. Cziczo, Z. Kanji, U. Lohmann, and O. Möhler, 2006: Solid ammonium sulfate aerosols as ice nuclei: A pathway for cirrus cloud formation. *Science*, **313**, 1770–1773, doi:10.1126/science.1129726.

Adler, G., T. Koop, C. Haspel, I. Taraniuk, T. Moise, I. Koren, R. H. Heiblum, and Y. Rudich, 2013: Formation of highly porous aerosol particles by atmospheric freeze-drying in ice clouds. *Proc. Natl. Acad. Sci. USA*, **110**, 20 414–20 419, doi:10.1073/pnas.1317209110.

——, C. Haspel, T. Moise, and Y. Rudich, 2014: Optical extinction of highly porous aerosol following atmospheric freeze drying. *J. Geophys. Res. Atmos.*, **119**, 6768–6787, doi:10.1002/2013JD021314.

Alpert, P., J. Aller, and D. Knopf, 2011: Ice nucleation from aqueous NaCl droplets with and without marine diatoms. *Atmos. Chem. Phys.*, **11**, 5539–5555, doi:10.5194/acp-11-5539-2011.

Ansmann, A., and Coauthors, 2008: Influence of Saharan dust on cloud glaciation in southern Morocco during the Saharan Mineral Dust Experiment. *J. Geophys. Res.*, **113**, D04210, doi:10.1029/2007JD008785.

Archuleta, C. M., P. J. DeMott, and S. M. Kreidenweis, 2005: Ice nucleation by surrogates for atmospheric mineral dust and mineral dust/sulfate particles at cirrus temperatures. *Atmos. Chem. Phys.*, **5**, 2617–2634, doi:10.5194/acp-5-2617-2005.

Ardon-Dryer, K., and Z. Levin, 2014: Ground-based measurements of immersion freezing in the eastern Mediterranean. *Atmos. Chem. Phys.*, **14**, 5217–5231, doi:10.5194/acp-14-5217-2014.

——, ——, and R. P. Lawson, 2011: Characteristics of immersion freezing nuclei at the South Pole station in Antarctica. *Atmos. Chem. Phys.*, **11**, 4015–4024, doi:10.5194/acp-11-4015-2011.

Atkinson, J. D., and Coauthors, 2013: The importance of feldspar for ice nucleation by mineral dust in mixed-phase clouds. *Nature*, **498**, 355–358, doi:10.1038/nature12278.

Auer, A., Jr., D. Veal, and J. Marwitz, 1969: Observations of ice crystal and ice nuclei concentrations in stable cap clouds. *J. Atmos. Sci.*, **26**, 1342–1343, doi:10.1175/1520-0469(1969)026<1342:OOICAI>2.0.CO;2.

aufm Kampe, H. J., and H. K. Weickmann, 1951: The effectiveness of natural and artificial aerosols as freezing nuclei. *J. Meteor.*, **8**, 283–288, doi:10.1175/1520-0469(1951)008<0283:TEONAA>2.0.CO;2.

Augustin, S., and Coauthors, 2013: Immersion freezing of birch pollen washing water. *Atmos. Chem. Phys.*, **13**, 10 989–11 003, doi:10.5194/acp-13-10989-2013.

Augustin-Bauditz, S., H. Wex, S. Kanter, M. Ebert, D. Niedermeier, F. Stolz, A. Prager, and F. Stratmann, 2014: The immersion mode ice nucleation behavior of mineral dusts: A comparison of different pure and surface modified dusts. *Geophys. Res. Lett.*, **41**, 7375–7382, doi:10.1002/2014GL061317.

——, ——, C. Denjean, S. Hartmann, J. Schneider, S. Schmidt, M. Ebert, and F. Stratmann, 2016: Laboratory-generated mixtures of mineral dust particles with biological substances: Characterization of the particle mixing state and immersion freezing behavior. *Atmos. Chem. Phys.*, **16**, 5531–5543, doi:10.5194/acp-16-5531-2016.

Baustian, K., M. Wise, and M. Tolbert, 2010: Depositional ice nucleation on solid ammonium sulfate and glutaric acid particles. *Atmos. Chem. Phys.*, **10**, 2307–2317, doi:10.5194/acp-10-2307-2010.

——, ——, E. Jensen, G. Schill, M. Freedman, and M. Tolbert, 2013: State transformations and ice nucleation in amorphous (semi-) solid organic aerosol. *Atmos. Chem. Phys.*, **13**, 5615–5628, doi:10.5194/acp-13-5615-2013.

Bigg, E. K., 1953: The formation of atmospheric ice crystals by the freezing of droplets. *Quart. J. Roy. Meteor. Soc.*, **79**, 510–519, doi:10.1002/qj.49707934207.

——, 1973: Ice nucleus concentrations in remote areas. *J. Atmos. Sci.*, **30**, 1153–1157, doi:10.1175/1520-0469(1973)030<1153:INCIRA>2.0.CO;2.

Bingemer, H., and Coauthors, 2012: Atmospheric ice nuclei in the Eyjafjallajökull volcanic ash plume. *Atmos. Chem. Phys.*, **12**, 857–867, doi:10.5194/acp-12-857-2012.

Bond, T. C., and Coauthors, 2013: Bounding the role of black carbon in the climate system: A scientific assessment. *J. Geophys. Res. Atmos.*, **118**, 5380–5552, doi:10.1002/jgrd.50171.

Boose, Y., and Coauthors, 2016a: Ice nucleating particle measurements at 241 K during winter months at 3580 m MSL in the Swiss Alps. *J. Atmos. Sci.*, **73**, 2203–2228, doi:10.1175/JAS-D-15-0236.1.

——, and Coauthors, 2016b: Ice nucleating particles in the Saharan Air Layer. *Atmos. Chem. Phys.*, **16**, 9067–9087, doi:10.5194/acp-16-9067-2016.

——, and Coauthors, 2016c: Heterogeneous ice nucleation on dust particles sourced from nine deserts worldwide—Part 1: Immersion freezing. *Atmos. Chem. Phys.*, **16**, 15 075–15 095, doi:10.5194/acp-16-15075-2016.

Boucher, O., and Coauthors, 2013: Clouds and aerosols. *Climate Change 2013: The Physical Science Basis*, T. F. Stocker et al., Eds., Cambridge University Press, 571–657.

Broadley, S. L., B. J. Murray, R. J. Herbert, J. D. Atkinson, S. Dobbie, T. L. Malkin, E. Condliffe, and L. Neve, 2012: Immersion mode heterogeneous ice nucleation by an illite rich powder representative of atmospheric mineral dust. *Atmos. Chem. Phys.*, **12**, 287–307, doi:10.5194/acp-12-287-2012.

Brooks, S. D., K. Suter, and L. Olivarez, 2014: Effects of chemical aging on the ice nucleation activity of soot and polycyclic aromatic hydrocarbon aerosols. *J. Phys. Chem.*, **118A**, 10 036–10 047, doi:10.1021/jp508809y.

Bühl, J., A. Ansmann, P. Seifert, H. Baars, and R. Engelmann, 2013: Toward a quantitative characterization of heterogeneous ice formation with lidar/radar: Comparison of CALIPSO/CloudSat with ground-based observations. *Geophys. Res. Lett.*, **40**, 4404–4408, doi:10.1002/grl.50792.

Cantrell, W., and A. Heymsfield, 2005: Production of ice in tropospheric clouds: A review. *Bull. Amer. Meteor. Soc.*, **86**, 795–807, doi:10.1175/BAMS-86-6-795.

Chen, J. P., A. Hazra, and Z. Levin, 2008: Parameterizing ice nucleation rates using contact angle and activation energy derived from laboratory data. *Atmos. Chem. Phys.*, **8**, 7431–7449, doi:10.5194/acp-8-7431-2008.

Chen, Y. L., P. J. DeMott, S. M. Kreidenweis, D. C. Rogers, and D. E. Sherman, 2000: Ice formation by sulfate and sulfuric acid aerosol particles under upper-tropospheric conditions. *J. Atmos. Sci.*, **57**, 3752–3766, doi:10.1175/1520-0469(2000)057<3752:IFBSAS>2.0.CO;2.

Chou, C., O. Stetzer, E. Weingartner, Z. Jurányi, Z. Kanji, and U. Lohmann, 2011: Ice nuclei properties within a Saharan dust event at the Jungfraujoch in the Swiss Alps. *Atmos. Chem. Phys.*, **11**, 4725–4738, doi:10.5194/acp-11-4725-2011.

——, and Coauthors, 2013: Effect of photochemical ageing on the ice nucleation properties of diesel and wood burning particles. *Atmos. Chem. Phys.*, **13**, 761–772, doi:10.5194/acp-13-761-2013.

Cober, S. G., and G. A. Isaac, 2012: Characterization of aircraft icing environments with supercooled large drops for application to commercial aircraft certification. *J. Appl. Meteor. Climatol.*, **51**, 265–284, doi:10.1175/JAMC-D-11-022.1.

——, ——, and J. W. Strapp, 2001: Characterizations of aircraft icing environments that include supercooled large drops. *J. Appl. Meteor.*, **40**, 1984–2002, doi:10.1175/1520-0450(2001)040<1984:COAIET>2.0.CO;2.

Conen, F., C. Morris, J. Leifeld, M. V. Yakutin, and C. Alewell, 2011: Biological residues define the ice nucleation properties of soil dust. *Atmos. Chem. Phys.*, **11**, 9643–9648, doi:10.5194/acp-11-9643-2011.

——, S. Henne, C. E. Morris, and C. Alewell, 2012: Atmospheric ice nucleators active $\geq -12^{\circ}$C can be quantified on PM_{10} filters. *Atmos. Meas. Tech.*, **5**, 321–327, doi:10.5194/amt-5-321-2012.

——, S. Rodríguez, C. Hüglin, S. Henne, E. Herrmann, N. Bukowiecki, and C. Alewell, 2015: Atmospheric ice nuclei at the high-altitude observatory Jungfraujoch, Switzerland. *Tellus*, **67B**, 25014, doi:10.3402/tellusb.v67.25014.

——, E. Stopelli, and L. Zimmermann, 2016: Clues that decaying leaves enrich Arctic air with ice nucleating particles. *Atmos. Environ.*, **129**, 91–94, doi:10.1016/j.atmosenv.2016.01.027.

Connolly, P. J., O. Möhler, P. R. Field, H. Saathoff, R. Burgess, T. Choularton, and M. Gallagher, 2009: Studies of heterogeneous freezing by three different desert dust samples. *Atmos. Chem. Phys.*, **9**, 2805–2824, doi:10.5194/acp-9-2805-2009.

Cooper, W. A., and G. Vali, 1981: The origin of ice in mountain cap clouds. *J. Atmos. Sci.*, **38**, 1244–1259, doi:10.1175/1520-0469(1981)038<1244:TOOIIM>2.0.CO;2.

Corbin, J., P. Rehbein, G. Evans, and J. Abbatt, 2012: Combustion particles as ice nuclei in an urban environment: Evidence from single-particle mass spectrometry. *Atmos. Environ.*, **51**, 286–292, doi:10.1016/j.atmosenv.2012.01.007.

Crawford, I., and Coauthors, 2012: Ice formation and development in aged, wintertime cumulus over the UK: Observations and modelling. *Atmos. Chem. Phys.*, **12**, 4963–4985, doi:10.5194/acp-12-4963-2012.

Creamean, J. M., and Coauthors, 2013: Dust and biological aerosols from the Sahara and Asia influence precipitation in the western U.S. *Science*, **339**, 1572–1578, doi:10.1126/science.1227279.

Cziczo, D. J., D. M. Murphy, P. K. Hudson, and D. S. Thomson, 2004: Single particle measurements of the chemical composition of cirrus ice residue during CRYSTAL-FACE. *J. Geophys. Res.*, **109**, D04201, doi:10.1029/2003JD004032.

——, K. D. Froyd, S. J. Gallavardin, O. Moehler, S. Benz, H. Saathoff, and D. M. Murphy, 2009a: Deactivation of ice nuclei due to atmospherically relevant surface coatings. *Environ. Res. Lett.*, **4**, 044013, doi:10.1088/1748-9326/4/4/044013.

——, and Coauthors, 2009b: Inadvertent climate modification due to anthropogenic lead. *Nat. Geosci.*, **2**, 333–336, doi:10.1038/ngeo499.

——, and Coauthors, 2013: Clarifying the dominant sources and mechanisms of cirrus cloud formation. *Science*, **340**, 1320–1324, doi:10.1126/science.1234145.

——, L. Ladino, Y. Boose, Z. A. Kanji, P. Kupiszewski, S. Lance, S. Mertes, and H. Wex, 2017: Measurements of ice nucleating particles and ice residuals. *Ice Formation and Evolution in Clouds and Precipitation: Measurement and Modeling Challenges*, *Meteor. Monogr.*, No. 58, Amer. Meteor. Soc., doi:10.1175/AMSMONOGRAPHS-D-16-0008.1.

Davies, P. L., 2014: Ice-binding proteins: A remarkable diversity of structures for stopping and starting ice growth. *Trends Biochem. Sci.*, **39**, 548–555, doi:10.1016/j.tibs.2014.09.005.

de Boer, G., H. Morrison, M. D. Shupe, and R. Hildner, 2011: Evidence of liquid dependent ice nucleation in high-latitude stratiform clouds from surface remote sensors. *Geophys. Res. Lett.*, **38**, L01803, doi:10.1029/2010GL046016.

DeMott, P. J., 1990: An exploratory study of ice nucleation by soot aerosols. *J. Appl. Meteor.*, **29**, 1072–1079, doi:10.1175/1520-0450(1990)029<1072:AESOIN>2.0.CO;2.

——, Y. Chen, S. Kreidenweis, D. Rogers, and D. E. Sherman, 1999: Ice formation by black carbon particles. *Geophys. Res. Lett.*, **26**, 2429–2432, doi:10.1029/1999GL900580.

——, D. J. Cziczo, A. J. Prenni, D. M. Murphy, S. M. Kreidenweis, D. S. Thomson, R. Borys, and D. C. Rogers, 2003a: Measurements of the concentration and composition of nuclei for cirrus formation. *Proc. Natl. Acad. Sci. USA*, **100**, 14 655–14 660, doi:10.1073/pnas.2532677100.

——, K. Sassen, M. R. Poellot, D. Baumgardner, D. C. Rogers, S. D. Brooks, A. J. Prenni, and S. M. Kreidenweis, 2003b: African dust aerosols as atmospheric ice nuclei. *Geophys. Res. Lett.*, **30**, 1732, doi:10.1029/2003GL017410.

——, and Coauthors, 2010: Predicting global atmospheric ice nuclei distributions and their impacts on climate. *Proc. Natl. Acad. Sci. USA*, **107**, 11 217–11 222, doi:10.1073/pnas.0910818107.

——, and Coauthors, 2011: Resurgence in ice nuclei measurement research. *Bull. Amer. Meteor. Soc.*, **92**, 1623–1635, doi:10.1175/2011BAMS3119.1.

——, and Coauthors, 2015: Integrating laboratory and field data to quantify the immersion freezing ice nucleation activity of mineral dust particles. *Atmos. Chem. Phys.*, **15**, 393–409, doi:10.5194/acp-15-393-2015.

——, and Coauthors, 2016: Sea spray aerosol as a unique source of ice nucleating particles. *Proc. Natl. Acad. Sci. USA*, **113**, 5797–5803, doi:10.1073/pnas.1514034112.

Dentener, F., and Coauthors, 2006: Emissions of primary aerosol and precursor gases in the years 2000 and 1750 prescribed data-sets for AeroCom. *Atmos. Chem. Phys.*, **6**, 4321–4344, doi:10.5194/acp-6-4321-2006.

Després, V. R., and Coauthors, 2012: Primary biological aerosol particles in the atmosphere: A review. *Tellus*, **64B**, doi:10.3402/tellusb.v64i0.15598.

Durant, A. J., and R. A. Shaw, 2005: Evaporation freezing by contact nucleation inside-out. *Geophys. Res. Lett.*, **32**, L20814, doi:10.1029/2005GL024175.

——, ——, W. I. Rose, Y. Mi, and G. G. J. Ernst, 2008: Ice nucleation and overseeding of ice in volcanic clouds. *J. Geophys. Res.*, **113**, D09206, doi:10.1029/2007JD009064.

Eidhammer, T., P. J. DeMott, and S. M. Kreidenweis, 2009: A comparison of heterogeneous ice nucleation parameterizations using a parcel model framework. *J. Geophys. Res.*, **114**, D06202, doi:10.1029/2008JD011095.

——, and Coauthors, 2010: Ice initiation by aerosol particles: Measured and predicted ice nuclei concentrations versus measured ice crystal concentrations in an orographic wave cloud. *J. Atmos. Sci.*, **67**, 2417–2436, doi:10.1175/2010JAS3266.1.

Emersic, C., P. J. Connolly, S. Boult, M. Campana, and Z. Li, 2015: Investigating the discrepancy between wet-suspension- and dry-dispersion-derived ice nucleation efficiency of mineral particles. *Atmos. Chem. Phys.*, **15**, 11 311–11 326, doi:10.5194/acp-15-11311-2015.

Engelstaedter, S., I. Tegen, and R. Washington, 2006: North African dust emissions and transport. *Earth-Sci. Rev.*, **79**, 73–100, doi:10.1016/j.earscirev.2006.06.004.

Ervens, B., and G. Feingold, 2013: Sensitivities of immersion freezing: Reconciling classical nucleation theory and deterministic expressions. *Geophys. Res. Lett.*, **40**, 3320–3324, doi:10.1002/grl.50580.

Field, P. R., and Coauthors, 2001: Ice nucleation in orographic wave clouds: Measurements made during INTACC. *Quart. J. Roy. Meteor. Soc.*, **127**, 1493–1512, doi:10.1002/qj.49712757502.

——, A. J. Heymsfield, B. J. Shipway, P. J. DeMott, K. A. Pratt, D. C. Rogers, J. Stith, and K. A. Prather, 2012: Ice in Clouds Experiment–Layer Clouds. Part II: Testing characteristics of heterogeneous ice formation in lee wave clouds. *J. Atmos. Sci.*, **69**, 1066–1079, doi:10.1175/JAS-D-11-026.1.

——, and Coauthors, 2017: Secondary ice production: Current state of the science and recommendations for the future. *Ice Formation and Evolution in Clouds and Precipitation: Measurement and Modeling Challenges*, *Meteor. Monogr.*, No. 58, Amer. Meteor. Soc., doi:10.1175/AMSMONOGRAPHS-D-16-0014.1.

Flagan, R. C., and J. H. Seinfeld, 1988: Particle formation in combustion. *Fundamentals of Air Pollution Engineering*, Prentice Hall, 358–390.

Fletcher, N. H., 1959: On ice-crystal production by aerosol particles. *J. Meteor.*, **16**, 173–180, doi:10.1175/1520-0469(1959)016<0173:OICPBA>2.0.CO;2.

——, 1962: *The Physics of Rainclouds*. Cambridge University Press, 386 pp.

——, 1969: Active sites and ice crystal nucleation. *J. Atmos. Sci.*, **26**, 1266–1271, doi:10.1175/1520-0469(1969)026<1266:asaicn>2.0.co;2.

Fornea, A. P., S. D. Brooks, J. B. Dooley, and A. Saha, 2009: Heterogeneous freezing of ice on atmospheric aerosols containing ash, soot, and soil. *J. Geophys. Res.*, **114**, D13201, doi:10.1029/2009JD011958.

Freedman, M. A., 2015: Potential sites for ice nucleation on aluminosilicate clay minerals and related materials. *J. Phys. Chem. Lett.*, **6**, 3850–3858, doi:10.1021/acs.jpclett.5b01326.

Friedman, B., G. Kulkarni, J. Beranek, A. Zelenyuk, J. A. Thornton, and D. J. Cziczo, 2011: Ice nucleation and droplet formation by bare and coated soot particles. *J. Geophys. Res.*, **116**, D17203, doi:10.1029/2011JD015999.

Fröhlich-Nowoisky, J., T. C. J. Hill, B. G. Pummer, G. D. Franc, and U. Pöschl, 2015: Ice nucleation activity in the widespread soil fungus Mortierella alpina. *Biogeosciences*, **12**, 1057–1071, doi:10.5194/bg-12-1057-2015.

Fukuta, N., and R. C. Schaller, 1982: Ice nucleation by aerosol-particles: Theory of condensation-freezing nucleation. *J. Atmos. Sci.*, **39**, 648–655, doi:10.1175/1520-0469(1982)039<0648:INBAPT>2.0.CO;2.

Garcia, E., T. C. Hill, A. J. Prenni, P. J. DeMott, G. D. Franc, and S. M. Kreidenweis, 2012: Biogenic ice nuclei in boundary layer air over two U.S. High Plains agricultural regions. *J. Geophys. Res.*, **117**, D18209, doi:10.1029/2012JD018343.

Garimella, S., D. A. Rothenberg, M. J. Wolf, R. O. David, Z. A. Kanji, C. Wang, M. Roesch, and D. J. Cziczo, 2017: Uncertainty in counting ice nucleating particles with continuous diffusion flow chambers. *Atmos. Chem. Phys. Discuss.*, **2017**, 1–28, doi:10.5194/acp-2016-1180.

Gibbs, A., M. Charman, W. Schwarzacher, and A. C. Rust, 2015: Immersion freezing of supercooled water drops containing glassy volcanic ash particles. *GeoResJ*, **7**, 66–69, doi:10.1016/j.grj.2015.06.002.

Gorbunov, B., A. Baklanov, N. Kakutkina, H. Windsor, and R. Toumi, 2001: Ice nucleation on soot particles. *J. Aerosol Sci.*, **32**, 199–215, doi:10.1016/S0021-8502(00)00077-X.

Govindarajan, A. G., and S. E. Lindow, 1988: Size of bacterial ice-nucleation sites measured in situ by radiation inactivation analysis. *Proc. Natl. Acad. Sci. USA*, **85**, 1334–1338, doi:10.1073/pnas.85.5.1334.

Grawe, S., S. Augustin-Bauditz, S. Hartmann, L. Hellner, J. B. C. Pettersson, A. Prager, F. Stratmann, and H. Wex, 2016: The immersion freezing behavior of ash particles from wood and brown coal burning. *Atmos. Chem. Phys.*, **16**, 13 911–13 928, doi:10.5194/acp-16-13911-2016.

Haag, W., B. Karcher, J. Strom, A. Minikin, U. Lohmann, J. Ovarlez, and A. Stohl, 2003: Freezing thresholds and cirrus cloud formation mechanisms inferred from in situ measurements of relative humidity. *Atmos. Chem. Phys.*, **3**, 1791–1806, doi:10.5194/acp-3-1791-2003.

Hallett, J., and S. Mossop, 1974: Production of secondary ice particles during the riming process. *Nature*, **249**, 26–28, doi:10.1038/249026a0.

Harrison, A. D., T. F. Whale, M. A. Carpenter, M. A. Holden, L. Neve, D. O'Sullivan, J. Vergara Temprado, and B. J. Murray, 2016: Not all feldspars are equal: A survey of ice nucleating properties across the feldspar group of minerals. *Atmos. Chem. Phys.*, **16**, 10 927–10 940, doi:10.5194/acp-16-10927-2016.

Hartmann, S., D. Niedermeier, J. Voigtländer, T. Clauss, R. A. Shaw, H. Wex, A. Kiselev, and F. Stratmann, 2011: Homogeneous and heterogeneous ice nucleation at LACIS: Operating principle and theoretical studies. *Atmos. Chem. Phys.*, **11**, 1753–1767, doi:10.5194/acp-11-1753-2011.

——, S. Augustin, T. Clauss, H. Wex, T. Santl Temkiv, J. Voigtländer, D. Niedermeier, and F. Stratmann, 2013: Immersion freezing of ice nucleating active protein complexes. *Atmos. Chem. Phys.*, **13**, 5751–5766, doi:10.5194/acp-13-5751-2013.

——, H. Wex, T. Clauss, S. Augustin-Bauditz, D. Niedermeier, M. Rösch, and F. Stratmann, 2016: Immersion freezing of kaolinite: Scaling with particle surface area. *J. Atmos. Sci.*, **73**, 263–278, doi:10.1175/JAS-D-15-0057.1.

Heymsfield, A. J., and P. Willis, 2014: Cloud conditions favoring secondary ice particle production in tropical maritime convection. *J. Atmos. Sci.*, **71**, 4500–4526, doi:10.1175/JAS-D-14-0093.1.

——, and Coauthors, 2017: Cirrus clouds. *Ice Formation and Evolution in Clouds and Precipitation: Measurement and Modeling Challenges*, *Meteor. Monogr.*, No. 58, Amer. Meteor. Soc., doi:10.1175/AMSMONOGRAPHS-D-16-0010.1.

Hill, T. C. J., P. J. DeMott, Y. Tobo, J. Fröhlich-Nowoisky, B. F. Moffett, G. D. Franc, and S. M. Kreidenweis, 2016: Sources of organic ice nucleating particles in soils. *Atmos. Chem. Phys.*, **16**, 7195–7211, doi:10.5194/acp-16-7195-2016.

Hiranuma, N., N. Hoffmann, A. Kiselev, A. Dreyer, K. Zhang, G. Kulkarni, T. Koop, and O. Mohler, 2014a: Influence of surface morphology on the immersion mode ice nucleation efficiency of hematite particles. *Atmos. Chem. Phys.*, **14**, 2315–2324, doi:10.5194/acp-14-2315-2014.

——, and Coauthors, 2014b: A comprehensive parameterization of heterogeneous ice nucleation of dust surrogate: Laboratory study with hematite particles and its application to atmospheric models. *Atmos. Chem. Phys.*, **14**, 13 145–13 158, doi:10.5194/acp-14-13145-2014.

——, and Coauthors, 2015: Ice nucleation by cellulose and its potential contribution to ice formation in clouds. *Nat. Geosci.*, **8**, 273–277, doi:10.1038/ngeo2374.

Hoffmann, N., D. Duft, A. Kiselev, and T. Leisner, 2013a: Contact freezing efficiency of mineral dust aerosols studied in an electrodynamic balance: Quantitative size and temperature dependence for illite particles. *Faraday Discuss.*, **165**, 383–390, doi:10.1039/c3fd00033h.

——, A. Kiselev, D. Rzesanke, D. Duft, and T. Leisner, 2013b: Experimental quantification of contact freezing in an electrodynamic balance. *Atmos. Meas. Tech.*, **6**, 2373–2382, doi:10.5194/amt-6-2373-2013.

Hoose, C., and O. Möhler, 2012: Heterogeneous ice nucleation on atmospheric aerosols: A review of results from laboratory experiments. *Atmos. Chem. Phys.*, **12**, 9817–9854, doi:10.5194/acp-12-9817-2012.

——, U. Lohmann, R. Erdin, and I. Tegen, 2008: The global influence of dust mineralogical composition on heterogeneous ice nucleation in mixed-phase clouds. *Environ. Res. Lett.*, **3**, 025003, doi:10.1088/1748-9326/3/2/025003.

——, J. E. Kristjansson, and S. M. Burrows, 2010: How important is biological ice nucleation in clouds on a global scale? *Environ. Res. Lett.*, **5**, 024009, doi:10.1088/1748-9326/5/2/024009.

Hoyle, C., and Coauthors, 2011: Ice nucleation properties of volcanic ash from Eyjafjallajökull. *Atmos. Chem. Phys.*, **11**, 9911–9926, doi:10.5194/acp-11-9911-2011.

Huffman, J. A., and Coauthors, 2013: High concentrations of biological aerosol particles and ice nuclei during and after rain. *Atmos. Chem. Phys.*, **13**, 6151–6164, doi:10.5194/acp-13-6151-2013.

Ignatius, K., and Coauthors, 2016: Heterogeneous ice nucleation of viscous secondary organic aerosol produced from ozonolysis of α-pinene. *Atmos. Chem. Phys.*, **16**, 6495–6509, doi:10.5194/acp-16-6495-2016.

Kamphus, M., and Coauthors, 2010: Chemical composition of ambient aerosol, ice residues and cloud droplet residues in mixed-phase clouds: Single particle analysis during the Cloud and Aerosol Characterization Experiment (CLACE 6). *Atmos. Chem. Phys.*, **10**, 8077–8095, doi:10.5194/acp-10-8077-2010.

Kanji, Z. A., and J. P. Abbatt, 2006: Laboratory studies of ice formation via deposition mode nucleation onto mineral dust and n-hexane soot samples. *J. Geophys. Res.*, **111**, D16204, doi:10.1029/2005JD006766.

——, and J. P. D. Abbatt, 2010: Ice nucleation onto Arizona Test Dust at cirrus temperatures: Effect of temperature and aerosol size on onset relative humidity. *J. Phys. Chem.*, **114A**, 935–941, doi:10.1021/jp908661m.

——, O. Florea, and J. P. D. Abbatt, 2008: Ice formation via deposition nucleation on mineral dust and organics: Dependence of onset relative humidity on total particulate surface area. *Environ. Res. Lett.*, **3**, 025004, doi:10.1088/1748-9326/3/2/025004.

——, P. J. DeMott, O. Möhler, and J. P. D. Abbatt, 2011: Results from the University of Toronto continuous flow diffusion chamber at ICIS 2007: Instrument intercomparison and ice onsets for different aerosol types. *Atmos. Chem. Phys.*, **11**, 31–41, doi:10.5194/acp-11-31-2011.

——, A. Welti, C. Chou, O. Stetzer, and U. Lohmann, 2013: Laboratory studies of immersion and deposition mode ice nucleation of ozone aged mineral dust particles. *Atmos. Chem. Phys.*, **13**, 9097–9118, doi:10.5194/acp-13-9097-2013.

Kärcher, B., and U. Lohmann, 2003: A parameterization of cirrus cloud formation: Heterogeneous freezing. *J. Geophys. Res. Atmos.*, **108**, 4402, doi:10.1029/2002JD003220.

——, and P. Spichtinger, 2009: Cloud-controlling factors of cirrus. *Clouds in the Perturbed Climate System: Their Relationship to Energy Balance, Atmospheric Dynamics and Precipitation*, J. Heintzeberg and R. J. Charlson, Eds., MIT Press, 235–268.

——, O. Mohler, P. J. DeMott, S. Pechtl, and F. Yu, 2007: Insights into the role of soot aerosols in cirrus cloud formation. *Atmos. Chem. Phys.*, **7**, 4203–4227, doi:10.5194/acp-7-4203-2007.

——, B. Mayer, K. Gierens, U. Burkhardt, H. Mannstein, and R. Chatterjee, 2009: Aerodynamic contrails: Microphysics and optical properties. *J. Atmos. Sci.*, **66**, 227–243, doi:10.1175/2008JAS2768.1.

Kaufmann, L., C. Marcolli, J. Hofer, V. Pinti, C. R. Hoyle, and T. Peter, 2016: Ice nucleation efficiency of natural dust samples in the immersion mode. *Atmos. Chem. Phys.*, **16**, 11 177–11 206, doi:10.5194/acp-16-11177-2016.

Kay, J. E., and Coauthors, 2012: Exposing global cloud biases in the Community Atmosphere Model (CAM) using satellite observations and their corresponding instrument simulators. *J. Climate*, **25**, 5190–5207, doi:10.1175/JCLI-D-11-00469.1.

Kiselev, A., F. Bachmann, P. Pedevilla, S. J. Cox, A. Michaelides, D. Gerthsen, and T. Leisner, 2016: Active sites in heterogeneous ice nucleation—The example of K-rich feldspars. *Science*, **10**, doi:10.1126/science.aai8034.

Klein, S. A., and Coauthors, 2009: Intercomparison of model simulations of mixed-phase clouds observed during the ARM Mixed-Phase Arctic Cloud Experiment. I: Single-layer cloud. *Quart. J. Roy. Meteor. Soc.*, **135**, 979–1002, doi:10.1002/qj.416.

Knippertz, P., and J. Stuut, Eds., 2014: *Mineral Dust: A Key Player in the Earth System.* Springer, 509 pp.

Knopf, D. A., and T. Koop, 2006: Heterogeneous nucleation of ice on surrogates of mineral dust. *J. Geophys. Res.*, **111**, D12201, doi:10.1029/2005JD006894.

——, B. Wang, A. Laskin, R. C. Moffet, and M. K. Gilles, 2010: Heterogeneous nucleation of ice on anthropogenic organic particles collected in Mexico City. *Geophys. Res. Lett.*, **37**, L11803, doi:10.1029/2010GL043362.

——, P. A. Alpert, B. Wang, and J. Y. Aller, 2011: Stimulation of ice nucleation by marine diatoms. *Nat. Geosci.*, **4**, 88–90, doi:10.1038/ngeo1037.

Koehler, K. A., and Coauthors, 2009: Cloud condensation nuclei and ice nucleation activity of hydrophobic and hydrophilic soot particles. *Phys. Chem. Chem. Phys.*, **11**, 7906–7920, doi:10.1039/b905334b.

Kohn, M., U. Lohmann, A. Welti, and Z. A. Kanji, 2016: Immersion mode ice nucleation measurements with the new Portable Immersion Mode Cooling chAmber (PIMCA). *J. Geophys. Res. Atmos.*, **121**, 4713–4733, doi:10.1002/2016JD024761.

Koop, T., H. P. Ng, L. T. Molina, and M. J. Molina, 1998: A new optical technique to study aerosol phase transitions: The nucleation of ice from H_2SO_4 aerosols. *J. Phys. Chem.*, **102A**, 8924–8931, doi:10.1021/jp9828078.

——, B. P. Luo, A. Tsias, and T. Peter, 2000: Water activity as the determinant for homogeneous ice nucleation in aqueous solutions. *Nature*, **406**, 611–614, doi:10.1038/35020537.

Korolev, A., 2007: Limitations of the Wegener–Bergeron–Findeisen mechanism in the evolution of mixed-phase clouds. *J. Atmos. Sci.*, **64**, 3372–3375, doi:10.1175/JAS4035.1.

——, and P. R. Field, 2008: The effect of dynamics on mixed-phase clouds: Theoretical considerations. *J. Atmos. Sci.*, **65**, 66–86, doi:10.1175/2007JAS2355.1.

——, E. Emery, J. Strapp, S. Cober, G. Isaac, M. Wasey, and D. Marcotte, 2011: Small ice particles in tropospheric clouds: Fact or artifact? Airborne Icing Instrumentation Evaluation Experiment. *Bull. Amer. Meteor. Soc.*, **92**, 967–973, doi:10.1175/2010BAMS3141.1.

——, and Coauthors, 2017: Mixed-phase clouds: Progress and challenges. *Ice Formation and Evolution in Clouds and Precipitation: Measurement and Modeling Challenges*, Meteor. Monogr., No. 58, Amer. Meteor. Soc., doi:10.1175/AMSMONOGRAPHS-D-17-0001.1.

Krämer, M., and Coauthors, 2016: A microphysics guide to cirrus clouds—Part 1: Cirrus types. *Atmos. Chem. Phys.*, **16**, 3463–3483, doi:10.5194/acp-16-3463-2016.

Kuebbeler, M., U. Lohmann, J. Hendricks, and B. Kärcher, 2014: Dust ice nuclei effects on cirrus clouds. *Atmos. Chem. Phys.*, **14**, 3027–3046, doi:10.5194/acp-14-3027-2014.

Kulkarni, G., C. Sanders, K. Zhang, X. Liu, and C. Zhao, 2014: Ice nucleation of bare and sulfuric acid coated mineral dust particles and implication for cloud properties. *J. Geophys. Res. Atmos.*, **119**, 9993–10 011, doi:10.1002/2014JD021567.

——, and Coauthors, 2015a: Effects of crystallographic properties on the ice nucleation properties of volcanic ash particles. *Geophys. Res. Lett.*, **42**, 3048–3055, doi:10.1002/2015GL063270.

——, K. Zhang, C. Zhao, M. Nandasiri, V. Shutthanandan, X. Liu, J. Fast, and L. Berg, 2015b: Ice formation on nitric acid-coated dust particles: Laboratory and modeling studies. *J. Geophys. Res. Atmos.*, **120**, 7682–7698, doi:10.1002/2014JD022637.

Laaksonen, A., 2015: A unifying model for adsorption and nucleation of vapors on solid surfaces. *J. Phys. Chem.*, **119A**, 3736–3745, doi:10.1021/acs.jpca.5b00325.

Ladino, L. A., O. Stetzer, F. Lüönd, A. Welti, and U. Lohmann, 2011: Contact freezing experiments of kaolinite particles with cloud droplets. *J. Geophys. Res.*, **116**, D22202, doi:10.1029/2011JD015727.

——, S. Zhou, J. D. Yakobi-Hancock, D. Aljawhary, and J. P. D. Abbatt, 2014: Factors controlling the ice nucleating abilities of α-pinene SOA particles. *J. Geophys. Res. Atmos.*, **119**, 9041–9051, doi:10.1002/2014JD021578.

——, and Coauthors, 2016: Addressing the ice nucleating abilities of marine aerosol: A combination of deposition mode laboratory and field measurements. *Atmos. Environ.*, **132**, 1–10, doi:10.1016/j.atmosenv.2016.02.028.

——, A. Korolev, I. Heckmann, M. Wolde, A. Fridlind, and A. Ackerman, 2017: On the role of ice-nucleating aerosol in the formation of ice particles in tropical mesoscale convective systems. *Geophys. Res. Lett.*, **44**, 1574–1582, doi:10.1002/2016GL072455.

Ladino Moreno, L., O. Stetzer, and U. Lohmann, 2013: Contact freezing: A review of experimental studies. *Atmos. Chem. Phys.*, **13**, 9745–9769, doi:10.5194/acp-13-9745-2013.

Langham, E. J., and B. J. Mason, 1958: The heterogeneous and homogeneous nucleation of supercooled water. *Proc. Roy. Soc. London*, **247A**, 493–504, doi:10.1098/rspa.1958.0207.

Lasher-Trapp, S., D. C. Leon, P. J. DeMott, C. M. Villanueva-Birriel, A. V. Johnson, D. H. Moser, C. S. Tully, and W. Wu, 2016: A multisensor investigation of rime splintering in tropical maritime cumuli. *J. Atmos. Sci.*, **73**, 2547–2564, doi:10.1175/JAS-D-15-0285.1.

Lau, K. M., and H. T. Wu, 2003: Warm rain processes over tropical oceans and climate implications. *Geophys. Res. Lett.*, **30**, 2290, doi:10.1029/2003GL018567.

Lawson, R. P., S. Woods, and H. Morrison, 2015: The microphysics of ice and precipitation development in tropical cumulus clouds. *J. Atmos. Sci.*, **72**, 2429–2445, doi:10.1175/JAS-D-14-0274.1.

Levin, E., G. McMeeking, P. DeMott, C. McCluskey, C. Stockwell, R. Yokelson, and S. Kreidenweis, 2014: A new method to determine the number concentrations of refractory black carbon ice nucleating particles. *Aerosol Sci. Technol.*, **48**, 1264–1275, doi:10.1080/02786826.2014.977843.

Lienhard, D. M., and Coauthors, 2015: Viscous organic aerosol particles in the upper troposphere: Diffusivity-controlled water uptake and ice nucleation? *Atmos. Chem. Phys.*, **15**, 13 599–13 613, doi:10.5194/acp-15-13599-2015.

Lindow, S. E., D. C. Arny, and C. D. Upper, 1982: Bacterial ice nucleation: A factor in frost injury to plants. *Plant Physiol.*, **70**, 1084–1089, doi:10.1104/pp.70.4.1084.

Lindzen, R. S., 1990: Some coolness concerning global warming. *Bull. Amer. Meteor. Soc.*, **71**, 288–299, doi:10.1175/1520-0477(1990)071<0288:SCCGW>2.0.CO;2.

Lloyd, G., and Coauthors, 2015: The origins of ice crystals measured in mixed-phase clouds at the high-alpine site Jungfraujoch. *Atmos. Chem. Phys.*, **15**, 12 953–12 969, doi:10.5194/acp-15-12953-2015.

Lohmann, U., and J. Feichter, 2005: Global indirect aerosol effects: A review. *Atmos. Chem. Phys.*, **5**, 715–737, doi:10.5194/acp-5-715-2005.

——, and C. Hoose, 2009: Sensitivity studies of different aerosol indirect effects in mixed-phase clouds. *Atmos. Chem. Phys.*, **9**, 8917–8934, doi:10.5194/acp-9-8917-2009.

Lüönd, F., O. Stetzer, A. Welti, and U. Lohmann, 2010: Experimental study on the ice nucleation ability of size-selected kaolinite particles in the immersion mode. *J. Geophys. Res.*, **115**, D14201, doi:10.1029/2009JD012959.

Lupi, L., A. Hudait, and V. Molinero, 2014: Heterogeneous nucleation of ice on carbon surfaces. *J. Amer. Chem. Soc.*, **136**, 3156–3164, doi:10.1021/ja411507a.

Mamouri, R. E., and A. Ansmann, 2016: Potential of polarization lidar to provide profiles of CCN- and INP-relevant aerosol parameters. *Atmos. Chem. Phys.*, **16**, 5905–5931, doi:10.5194/acp-16-5905-2016.

Marcolli, C., 2014: Deposition nucleation viewed as homogeneous or immersion freezing in pores and cavities. *Atmos. Chem. Phys.*, **14**, 2071–2104, doi:10.5194/acp-14-2071-2014.

——, S. Gedamke, T. Peter, and B. Zobrist, 2007: Efficiency of immersion mode ice nucleation on surrogates of mineral dust. *Atmos. Chem. Phys.*, **7**, 5081–5091, doi:10.5194/acp-7-5081-2007.

Mason, R. H., and Coauthors, 2015a: Ice nucleating particles at a coastal marine boundary layer site: Correlations with aerosol type and meteorological conditions. *Atmos. Chem. Phys.*, **15**, 12 547–12 566, doi:10.5194/acp-15-12547-2015.

——, and Coauthors, 2015b: The micro-oriF_{ice} uniform deposit impactor–droplet freezing technique (MOUDI-DFT) for measuring concentrations of ice nucleating particles as a function of size: Improvements and initial validation. *Atmos. Meas. Tech.*, **8**, 2449–2462, doi:10.5194/amt-8-2449-2015.

McCluskey, C. S., and Coauthors, 2014: Characteristics of atmospheric ice nucleating particles associated with biomass burning in the US: Prescribed burns and wildfires. *J. Geophys. Res. Atmos.*, **119**, 10 458–10 470, doi:10.1002/2014JD021980.

Mertes, S., and Coauthors, 2007: Counterflow virtual impactor based collection of small ice particles in mixed-phase clouds for the physico-chemical characterization of tropospheric ice nuclei: Sampler description and first case study. *Aerosol Sci. Technol.*, **41**, 848–864, doi:10.1080/02786820701501881.

Meyers, M. P., P. J. Demott, and W. R. Cotton, 1992: New primary ice-nucleation parameterizations in an explicit cloud model. *J. Appl. Meteor.*, **31**, 708–721, doi:10.1175/1520-0450(1992)031<0708:NPINPI>2.0.CO;2.

Möhler, O., and Coauthors, 2003: Experimental investigation of homogeneous freezing of sulphuric acid particles in the aerosol chamber AIDA. *Atmos. Chem. Phys.*, **3**, 211–223, doi:10.5194/acp-3-211-2003.

——, C. Linke, H. Saathoff, M. Schnaiter, R. Wagner, A. Mangold, M. Krämer, and U. Schurath, 2005: Ice nucleation on flame soot aerosol of different organic carbon content. *Meteor. Z.*, **14**, 477–484, doi:10.1127/0941-2948/2005/0055.

——, and Coauthors, 2006: Efficiency of the deposition mode ice nucleation on mineral dust particles. *Atmos. Chem. Phys.*, **6**, 3007–3021, doi:10.5194/acp-6-3007-2006.

——, and Coauthors, 2008: The effect of organic coating on the heterogeneous ice nucleation efficiency of mineral dust aerosols. *Environ. Res. Lett.*, **3**, 025007, doi:10.1088/1748-9326/3/2/025007.

Mossop, S., 1970: Concentrations of ice crystals in clouds. *Bull. Amer. Meteor. Soc.*, **51**, 474–479, doi:10.1175/1520-0477(1970)051<0474:COICIC>2.0.CO;2.

Mülmenstädt, J., O. Sourdeval, J. Delanoe, and J. Quaas, 2015: Frequency of occurrence of rain from liquid-, mixed-, and ice-phase clouds derived from A-Train satellite retrievals. *Geophys. Res. Lett.*, **42**, 6502–6509, doi:10.1002/2015GL064604.

Murphy, D. M., and T. Koop, 2005: Review of the vapour pressures of ice and supercooled water for atmospheric applications. *Quart. J. Roy. Meteor. Soc.*, **131**, 1539–1565, doi:10.1256/qj.04.94.

Murray, B. J., and Coauthors, 2010: Heterogeneous nucleation of ice particles on glassy aerosols under cirrus conditions. *Nat. Geosci.*, **3**, 233–237, doi:10.1038/ngeo817.

——, S. L. Broadley, T. W. Wilson, J. D. Atkinson, and R. H. Wills, 2011: Heterogeneous freezing of water droplets containing kaolinite particles. *Atmos. Chem. Phys.*, **11**, 4191–4207, doi:10.5194/acp-11-4191-2011.

——, D. O'Sullivan, J. D. Atkinson, and M. E. Webb, 2012: Ice nucleation by particles immersed in supercooled cloud droplets. *Chem. Soc. Rev.*, **41**, 6519–6554, doi:10.1039/c2cs35200a.

Nagare, B., C. Marcolli, A. Welti, O. Stetzer, and U. Lohmann, 2016: Comparing contact and immersion freezing from continuous flow diffusion chambers. *Atmos. Chem. Phys.*, **16**, 8899–8914, doi:10.5194/acp-16-8899-2016.

Niedermeier, D., and Coauthors, 2010: Heterogeneous freezing of droplets with immersed mineral dust particles—Measurements and parameterization. *Atmos. Chem. Phys.*, **10**, 3601–3614, doi:10.5194/acp-10-3601-2010.

——, and Coauthors, 2011a: Experimental study of the role of physicochemical surface processing on the IN ability of mineral dust particles. *Atmos. Chem. Phys.*, **11**, 11 131–11 144, doi:10.5194/acp-11-11131-2011.

——, R. A. Shaw, S. Hartmann, H. Wex, T. Clauss, J. Voigtländer, and F. Stratmann, 2011b: Heterogeneous ice nucleation: Exploring the transition from stochastic to singular freezing behavior. *Atmos. Chem. Phys.*, **11**, 8767–8775, doi:10.5194/acp-11-8767-2011.

——, B. Ervens, T. Clauss, J. Voigtländer, H. Wex, S. Hartmann, and F. Stratmann, 2014: A computationally efficient description of heterogeneous freezing: A simplified version of the Soccer ball model. *Geophys. Res. Lett.*, **41**, 736–741, doi:10.1002/2013GL058684.

——, S. Augustin-Bauditz, S. Hartmann, H. Wex, K. Ignatius, and F. Stratmann, 2015: Can we define an asymptotic value for the ice active surface site density for heterogeneous ice nucleation? *J. Geophys. Res. Atmos.*, **120**, 5036–5046, doi:10.1002/2014JD022814.

Niehaus, J., and W. Cantrell, 2015: Contact freezing of water by salts. *J. Phys. Chem. Lett.*, **6**, 3490–3495, doi:10.1021/acs.jpclett.5b01531.

——, K. W. Bunker, S. China, A. Kostinski, C. Mazzoleni, and W. Cantrell, 2014: A technique to measure ice nuclei in the contact mode. *J. Atmos. Oceanic Technol.*, **31**, 913–922, doi:10.1175/JTECH-D-13-00156.1.

Niemand, M., and Coauthors, 2012: A particle-surface-area-based parameterization of immersion freezing on desert dust particles. *J. Atmos. Sci.*, **69**, 3077–3092, doi:10.1175/JAS-D-11-0249.1.

O'Sullivan, D., and Coauthors, 2014: Ice nucleation by fertile soil dusts: Relative importance of mineral and biogenic components. *Atmos. Chem. Phys.*, **14**, 1853–1867, doi:10.5194/acp-14-1853-2014.

——, B. J. Murray, J. F. Ross, T. F. Whale, H. C. Price, J. D. Atkinson, N. S. Umo, and M. E. Webb, 2015: The relevance of nanoscale biological fragments for ice nucleation in clouds. *Sci. Rep.*, **5**, 8082, doi:10.1038/srep08082.

——, ——, ——, and M. E. Webb, 2016: The adsorption of fungal ice-nucleating proteins on mineral dusts: A terrestrial reservoir of atmospheric ice-nucleating particles. *Atmos. Chem. Phys.*, **16**, 7879–7887, doi:10.5194/acp-16-7879-2016.

Pandey, R., and Coauthors, 2016: Ice-nucleating bacteria control the order and dynamics of interfacial water. *Sci. Adv.*, **2**, e1501630, doi:10.1126/sciadv.1501630.

Peckhaus, A., A. Kiselev, T. Hiron, M. Ebert, and T. Leisner, 2016: A comparative study of K-rich and Na/Ca-rich feldspar ice-nucleating particles in a nanoliter droplet freezing assay. *Atmos. Chem. Phys.*, **16**, 11 477–11 496, doi:10.5194/acp-16-11477-2016.

Pedevilla, P., S. J. Cox, B. Slater, and A. Michaelides, 2016: Can ice-like structures form on non-ice-like substrates? The example of the k feldspar microcline. *J. Phys. Chem.*, **120C**, 6704–6713, doi:10.1021/acs.jpcc.6b01155.

Peng, L., J. R. Snider, and Z. Wang, 2015: Ice crystal concentrations in wave clouds: Dependencies on temperature, $D > 0.5$ μm aerosol particle concentration, and duration of cloud processing. *Atmos. Chem. Phys.*, **15**, 6113–6125, doi:10.5194/acp-15-6113-2015.

Petters, M. D., and T. P. Wright, 2015: Revisiting ice nucleation from precipitation samples. *Geophys. Res. Lett.*, **42**, 8758–8766, doi:10.1002/2015GL065733.

——, and Coauthors, 2009: Ice nuclei emissions from biomass burning. *J. Geophys. Res.*, **114**, D07209, doi:10.1029/2008JD011532.

Phillips, V. T. J., P. J. DeMott, and C. Andronache, 2008: An empirical parameterization of heterogeneous ice nucleation for multiple chemical species of aerosol. *J. Atmos. Sci.*, **65**, 2757–2783, doi:10.1175/2007JAS2546.1.

——, ——, ——, K. A. Pratt, K. A. Prather, R. Subramanian, and C. Twohy, 2013: Improvements to an empirical parameterization of heterogeneous ice nucleation and its comparison with observations. *J. Atmos. Sci.*, **70**, 378–409, doi:10.1175/JAS-D-12-080.1.

Polen, M., E. Lawlis, and R. C. Sullivan, 2016: The unstable ice nucleation properties of Snomax bacterial particles. *J. Geophys. Res. Atmos.*, **121**, 11 666–11 678, doi:10.1002/2016JD025251.

Popovicheva, O., E. Kireeva, N. Persiantseva, T. Khokhlova, N. Shonija, V. Tishkova, and B. Demirdjian, 2008: Effect of soot on immersion freezing of water and possible atmospheric implications. *Atmos. Res.*, **90**, 326–337, doi:10.1016/j.atmosres.2008.08.004.

Prather, K. A., and Coauthors, 2013: Bringing the ocean into the laboratory to probe the chemical complexity of sea spray aerosol. *Proc. Natl. Acad. Sci. USA*, **110**, 7550–7555, doi:10.1073/pnas.1300262110.

Pratt, K. A., and Coauthors, 2009: In situ detection of biological particles in cloud ice-crystals. *Nat. Geosci.*, **2**, 398–401, doi:10.1038/ngeo521.

Prenni, A. J., P. J. Demott, D. C. Rogers, S. M. Kreidenweis, G. M. McFarquhar, G. Zhang, and M. R. Poellot, 2009a: Ice nuclei characteristics from M-PACE and their relation to ice formation in clouds. *Tellus*, **61B**, 436–448, doi:10.1111/j.1600-0889.2009.00415.x.

——, M. D. Petters, A. Faulhaber, C. M. Carrico, P. J. Ziemann, S. M. Kreidenweis, and P. J. DeMott, 2009b: Heterogeneous ice nucleation measurements of secondary organic aerosol generated from ozonolysis of alkenes. *Geophys. Res. Lett.*, **36**, L06808, doi:10.1029/2008GL036957.

——, P. J. DeMott, A. P. Sullivan, R. C. Sullivan, S. M. Kreidenweis, and D. C. Rogers, 2012: Biomass burning as a potential source for atmospheric ice nuclei: Western wildfires and prescribed burns. *Geophys. Res. Lett.*, **39**, L11805, doi:10.1029/2012GL051915.

——, and Coauthors, 2013: The impact of rain on ice nuclei populations at a forested site in Colorado. *Geophys. Res. Lett.*, **40**, 227–231, doi:10.1029/2012GL053953.

Prospero, J. M., 1999: Long-range transport of mineral dust in the global atmosphere: Impact of African dust on the environment of the southeastern United States. *Proc. Natl. Acad. Sci. USA*, **96**, 3396–3403, doi:10.1073/pnas.96.7.3396.

——, P. Ginoux, O. Torres, S. E. Nicholson, and T. E. Gill, 2002: Environmental characterization of global sources of atmospheric soil dust identified with the Nimbus 7 Total Ozone Mapping Spectrometer (TOMS) absorbing aerosol product. *Rev. Geophys.*, **40**, 1002, doi:10.1029/2000RG000095.

Pruppacher, H. R., and J. D. Klett, 1997: *Microphysics of Clouds and Precipitation.* 2nd ed. Kluwer, 976 pp.

Pummer, B. G., H. Bauer, J. Bernardi, S. Bleicher, and H. Grothe, 2012: Suspendable macromolecules are responsible for ice nucleation activity of birch and conifer pollen. *Atmos. Chem. Phys.*, **12**, 2541–2550, doi:10.5194/acp-12-2541-2012.

——, and Coauthors, 2015: Ice nucleation by water-soluble macromolecules. *Atmos. Chem. Phys.*, **15**, 4077–4091, doi:10.5194/acp-15-4077-2015.

Rasmussen, R., and Coauthors, 2006: New ground deicing hazard associated with freezing drizzle ingestion by jet engines. *J. Aircr.*, **43**, 1448–1457, doi:10.2514/1.20799.

Reitz, P., and Coauthors, 2011: Surface modification of mineral dust particles by sulphuric acid processing: Implications for ice nucleation abilities. *Atmos. Chem. Phys.*, **11**, 7839–7858, doi:10.5194/acp-11-7839-2011.

Richardson, M. S., and Coauthors, 2007: Measurements of heterogeneous ice nuclei in the western United States in springtime and their relation to aerosol characteristics. *J. Geophys. Res.*, **112**, D02209, doi:10.1029/2006JD007500.

Rogers, D. C., 1988: Development of a continuous flow thermal gradient diffusion chamber for ice nucleation studies. *Atmos. Res.*, **22**, 149–181, doi:10.1016/0169-8095(88)90005-1.

Rogers, R. R., and M. K. Yau, 1989: *A Short Course in Cloud Physics.* 3rd ed. International Series in Natural Philosophy, Vol. 113, Pergamon Press, 290 pp.

Rosinski, J., P. L. Haagenson, C. T. Nagamoto, and F. Parungo, 1987: Nature of ice-forming nuclei in marine air masses. *J. Aerosol Sci.*, **18**, 291–309, doi:10.1016/0021-8502(87)90024-3.

Salam, A., U. Lohmann, and G. Lesins, 2007: Ice nucleation of ammonia gas exposed montmorillonite mineral dust particles. *Atmos. Chem. Phys.*, **7**, 3923–3931, doi:10.5194/acp-7-3923-2007.

Santachiara, G., L. Di Matteo, F. Prodi, and F. Belosi, 2010: Atmospheric particles acting as ice forming nuclei in different size ranges. *Atmos. Res.*, **96**, 266–272, doi:10.1016/j.atmosres.2009.08.004.

Savre, J., and A. M. L. Ekman, 2015: Large-eddy simulation of three mixed-phase cloud events during ISDAC: Conditions for persistent heterogeneous ice formation. *J. Geophys. Res. Atmos.*, **120**, 7699–7725, doi:10.1002/2014JD023006.

Schill, G. P., and M. A. Tolbert, 2014: Heterogeneous ice nucleation on simulated sea-spray aerosol using Raman microscopy. *J. Phys. Chem.*, **118C**, 29 234–29 241, doi:10.1021/jp505379j.

——, D. O. De Haan, and M. A. Tolbert, 2014: Heterogeneous ice nucleation on simulated secondary organic aerosol. *Environ. Sci. Technol.*, **48**, 1675–1682, doi:10.1021/es4046428.

——, K. Genareau, and M. Tolbert, 2015a: Deposition and immersion mode nucleation of ice by three distinct samples of volcanic ash using Raman spectroscopy. *Atmos. Chem. Phys.*, **15**, 7523–7536, doi:10.5194/acp-15-7523-2015.

Schill, S. R., and Coauthors, 2015b: The impact of aerosol particle mixing state on the hygroscopicity of sea spray aerosol. ACS *Cent. Sci.*, **1**, 132–141, doi:10.1021/acscentsci.5b00174.

Schrod, J., A. Danielczok, D. Weber, M. Ebert, E. S. Thomson, and H. G. Bingemer, 2016: Re-evaluating the Frankfurt isothermal static diffusion chamber for ice nucleation. *Atmos. Meas. Tech.*, **9**, 1313–1324, doi:10.5194/amt-9-1313-2016.

Seifert, P., and Coauthors, 2011: Ice formation in ash-influenced clouds after the eruption of the Eyjafjallajokull volcano in April 2010. *J. Geophys. Res.*, **116**, D00U04, doi:10.1029/2011JD015702.

Shaw, R. A., A. J. Durant, and Y. Mi, 2005: Heterogeneous surface crystallization observed in undercooled water. *J. Phys. Chem.*, **109B**, 9865–9868, doi:10.1021/jp0506336.

Shilling, J., T. Fortin, and M. Tolbert, 2006: Depositional ice nucleation on crystalline organic and inorganic solids. *J. Geophys. Res.*, **111**, D12204, doi:10.1029/2005JD006664.

Siebesma, A. P., and Coauthors, 2009: Cloud-controlling factors. *Clouds in the Perturbed Climate System: Their Relationship to Energy Balance, Atmospheric Dynamics and Precipitation*, J. Heintzeberg and R. J. Charlson, Eds., MIT Press, 269–290.

Sihvonen, S. K., G. P. Schill, N. A. Lyktey, D. P. Veghte, M. A. Tolbert, and M. A. Freedman, 2014: Chemical and physical transformations of aluminosilicate clay minerals due to acid treatment and consequences for heterogeneous ice nucleation. *J. Phys. Chem.*, **118A**, 8787–8796, doi:10.1021/jp504846g.

Spichtinger, P., and D. J. Cziczo, 2010: Impact of heterogeneous ice nuclei on homogeneous freezing events in cirrus clouds. *J. Geophys. Res.*, **115**, D14208, doi:10.1029/2009JD012168.

Steinke, I., and Coauthors, 2011: Ice nucleation properties of fine ash particles from the Eyjafjallajökull eruption in April 2010. *Atmos. Chem. Phys.*, **11**, 12 945–12 958, doi:10.5194/acp-11-12945-2011.

Stith, J., C. Twohy, P. DeMott, D. Baumgardner, T. Campos, R. Gao, and J. Anderson, 2011: Observations of ice nuclei and heterogeneous freezing in a western Pacific extratropical storm. *Atmos. Chem. Phys.*, **11**, 6229–6243, doi:10.5194/acp-11-6229-2011.

Sullivan, R. C., and Coauthors, 2010b: Irreversible loss of ice nucleation active sites in mineral dust particles caused by sulphuric acid condensation. *Atmos. Chem. Phys.*, **10**, 11 471–11 487, doi:10.5194/acp-10-11471-2010.

——, L. Minambres, P. J. DeMott, A. J. Prenni, C. M. Carrico, E. J. T. Levin, and S. M. Kreidenweis, 2010a: Chemical processing does not always impair heterogeneous ice nucleation of mineral dust particles. *Geophys. Res. Lett.*, **37**, L24805, doi:10.1029/2010GL045540.

Suzanne, J., D. Ferry, O. Popovitcheva, and N. K. Shonija, 2003: Ice nucleation by kerosene soot under upper tropospheric conditions. *Can. J. Phys.*, **81**, 423–429, doi:10.1139/p03-004.

Tan, I., T. Storelvmo, and M. D. Zelinka, 2016: Observational constraints on mixed-phase clouds imply higher climate sensitivity. *Science*, **352**, 224–227, doi:10.1126/science.aad5300.

Thomson, E. S., X. Kong, P. Papagiannakopoulos, and J. B. C. Pettersson, 2015: Deposition-mode ice nucleation reexamined at temperatures below 200 K. *Atmos. Chem. Phys.*, **15**, 1621–1632, doi:10.5194/acp-15-1621-2015.

Tobo, Y., and Coauthors, 2013: Biological aerosol particles as a key determinant of ice nuclei populations in a forest ecosystem. *J. Geophys. Res. Atmos.*, **118**, 10 100–10 110, doi:10.1002/jgrd.50801.

——, P. DeMott, T. Hill, A. Prenni, N. Swoboda-Colberg, G. Franc, and S. Kreidenweis, 2014: Organic matter matters for ice nuclei of agricultural soil origin. *Atmos. Chem. Phys.*, **14**, 8521–8531, doi:10.5194/acp-14-8521-2014.

Trainer, M. G., O. B. Toon, and M. A. Tolbert, 2009: Measurements of depositional ice nucleation on insoluble substrates at low temperatures: Implications for Earth and Mars. *J. Phys. Chem.*, **113C**, 2036–2040, doi:10.1021/jp805140p.

Turner, M. A., F. Arellano, and L. M. Kozloff, 1990: Three separate classes of bacterial ice nucleation structures. *J. Bacteriol.*, **172**, 2521–2526, doi:10.1128/jb.172.5.2521-2526.1990.

——, ——, and ——, 1991: Components of ice nucleation structures of bacteria. *J. Bacteriol.*, **173**, 6515–6527, doi:10.1128/jb.173.20.6515-6527.1991.

Twohy, C. H., and Coauthors, 2010: Relationships of biomass-burning aerosols to ice in orographic wave clouds. *J. Atmos. Sci.*, **67**, 2437–2450, doi:10.1175/2010JAS3310.1.

Umo, N. S., and Coauthors, 2015: Ice nucleation by combustion ash particles at conditions relevant to mixed-phase clouds. *Atmos. Chem. Phys.*, **15**, 5195–5210, doi:10.5194/acp-15-5195-2015.

Vali, G., 1971: Quantitative evaluation of experimental results on heterogeneous freezing nucleation of supercooled liquids. *J. Atmos. Sci.*, **28**, 402–409, doi:10.1175/1520-0469(1971)028<0402:qeoera>2.0.co;2.

——, 1994: Freezing rate due to heterogeneous nucleation. *J. Atmos. Sci.*, **51**, 1843–1856, doi:10.1175/1520-0469(1994)051<1843:FRDTHN>2.0.CO;2.

——, 2008: Repeatability and randomness in heterogeneous freezing nucleation. *Atmos. Chem. Phys.*, **8**, 5017–5031, doi:10.5194/acp-8-5017-2008.

——, 2014: Interpretation of freezing nucleation experiments: Singular and stochastic; sites and surfaces. *Atmos. Chem. Phys.*, **14**, 5271–5294, doi:10.5194/acp-14-5271-2014.

——, and J. R. Snider, 2015: Time-dependent freezing rate parcel model. *Atmos. Chem. Phys.*, **15**, 2071–2079, doi:10.5194/acp-15-2071-2015.

——, P. J. DeMott, O. Moehler, and T. F. Whale, 2015: Technical Note: A proposal for ice nucleation terminology. *Atmos. Chem. Phys.*, **15**, 10 263–10 270, doi:10.5194/acp-15-10263-2015.

Vonnegut, B., 1947: The nucleation of ice formation by silver iodide. *J. Appl. Phys.*, **18**, 593–595, doi:10.1063/1.1697813.

Wagner, R., and O. Möhler, 2013: Heterogeneous ice nucleation ability of crystalline sodium chloride dihydrate particles. *J. Geophys. Res. Atmos.*, **118**, 4610–4622, doi:10.1002/jgrd.50325.

——, ——, H. Saathoff, M. Schnaiter, and T. Leisner, 2010: High variability of the heterogeneous ice nucleation potential of oxalic acid dihydrate and sodium oxalate. *Atmos. Chem. Phys.*, **10**, 7617–7641, doi:10.5194/acp-10-7617-2010.

——, and Coauthors, 2012: Ice cloud processing of ultra-viscous/glassy aerosol particles leads to enhanced ice nucleation ability. *Atmos. Chem. Phys.*, **12**, 8589–8610, doi:10.5194/acp-12-8589-2012.

——, O. Möhler, H. Saathoff, and M. Schnaiter, 2014: Enhanced high-temperature ice nucleation ability of crystallized aerosol particles after preactivation at low temperature. *J. Geophys. Res. Atmos.*, **119**, 8212–8230, doi:10.1002/2014JD021741.

——, A. Kiselev, O. Möhler, H. Saathoff, and I. Steinke, 2016: Pre-activation of ice-nucleating particles by the pore condensation and freezing mechanism. *Atmos. Chem. Phys.*, **16**, 2025–2042, doi:10.5194/acp-16-2025-2016.

Wang, B., A. T. Lambe, P. Massoli, T. B. Onasch, P. Davidovits, D. R. Worsnop, and D. A. Knopf, 2012: The deposition ice nucleation and immersion freezing potential of amorphous secondary organic aerosol: Pathways for ice and mixed-phase cloud formation. *J. Geophys. Res.*, **117**, D16209, doi:10.1029/2012JD018063.

——, D. A. Knopf, S. China, B. W. Arey, T. H. Harder, M. K. Gilles, and A. Laskin, 2016: Direct observation of ice nucleation events on individual atmospheric particles. *Phys. Chem. Chem. Phys.*, **18**, 29 721–29 731, doi:10.1039/C6CP05253C.

Wang, X., and Coauthors, 2015: Microbial control of sea spray aerosol composition: A tale of two blooms. ACS *Cent. Sci.*, **1**, 124–131, doi:10.1021/acscentsci.5b00148.

Welti, A., F. Lüönd, O. Stetzer, and U. Lohmann, 2009: Influence of particle size on the ice nucleating ability of mineral dusts. *Atmos. Chem. Phys.*, **9**, 6705–6715, doi:10.5194/acp-9-6705-2009.

——, ——, Z. A. Kanji, O. Stetzer, and U. Lohmann, 2012: Time dependence of immersion freezing: An experimental study on size selected kaolinite particles. *Atmos. Chem. Phys.*, **12**, 9893–9907, doi:10.5194/acp-12-9893-2012.

——, Z. A. Kanji, O. Stetzer, U. Lohmann, and F. Lüönd, 2014: Exploring the mechanisms of ice nucleation on kaolinite: From deposition nucleation to condensation freezing. *J. Atmos. Sci.*, **71**, 16–36, doi:10.1175/JAS-D-12-0252.1.

Westbrook, C. D., and A. J. Illingworth, 2013: The formation of ice in a long-lived supercooled layer cloud. *Quart. J. Roy. Meteor. Soc.*, **139**, 2209–2221, doi:10.1002/qj.2096.

Wex, H., and Coauthors, 2014: Kaolinite particles as ice nuclei: Learning from the use of different kaolinite samples and different coatings. *Atmos. Chem. Phys.*, **14**, 5529–5546, doi:10.5194/acp-14-5529-2014.

——, and Coauthors, 2015: Intercomparing different devices for the investigation of ice nucleating particles using Snomax as test substance. *Atmos. Chem. Phys.*, **15**, 1463–1485, doi:10.5194/acp-15-1463-2015.

Wilson, T. W., and Coauthors, 2012: Glassy aerosols with a range of compositions nucleate ice heterogeneously at cirrus temperatures. *Atmos. Chem. Phys.*, **12**, 8611–8632, doi:10.5194/acp-12-8611-2012.

——, and Coauthors, 2015: A marine biogenic source of atmospheric ice-nucleating particles. *Nature*, **525**, 234–238, doi:10.1038/nature14986.

Wise, M. E., K. J. Baustian, T. Koop, M. A. Freedman, E. J. Jensen, and M. A. Tolbert, 2012: Depositional ice nucleation onto crystalline hydrated NaCl particles: A new mechanism for ice formation in the troposphere. *Atmos. Chem. Phys.*, **12**, 1121–1134, doi:10.5194/acp-12-1121-2012.

Wright, T. P., and M. D. Petters, 2013: The role of time in heterogeneous freezing nucleation. *J. Geophys. Res. Atmos.*, **118**, 3731–3743, doi:10.1002/jgrd.50365.

——, ——, J. D. Hader, T. Morton, and A. L. Holder, 2013: Minimal cooling rate dependence of ice nuclei activity in the immersion mode. *J. Geophys. Res. Atmos.*, **118**, 10 535–10 543, doi:10.1002/jgrd.50810.

Yakobi-Hancock, J. D., L. A. Ladino, and J. P. D. Abbatt, 2013: Feldspar minerals as efficient deposition ice nuclei. *Atmos. Chem. Phys.*, **13**, 11 175–11 185, doi:10.5194/acp-13-11175-2013.

Zimmermann, F., S. Weinbruch, L. Schütz, H. Hofmann, M. Ebert, K. Kandler, and A. Worringen, 2008: Ice nucleation properties of the most abundant mineral dust phases. *J. Geophys. Res.*, **113**, D23204, doi:10.1029/2008JD010655.

Zobrist, B., and Coauthors, 2006: Oxalic acid as a heterogeneous ice nucleus in the upper troposphere and its indirect aerosol effect. *Atmos. Chem. Phys.*, **6**, 3115–3129, doi:10.5194/acp-6-3115-2006.

Zolles, T., J. Burkart, T. Haeusler, B. Pummer, R. Hitzenberger, and H. Grothe, 2015: Identification of ice nucleation active sites on feldspar dust particles. *J. Phys. Chem.*, **119A**, 2692–2700, doi:10.1021/jp509839x.