# A BLUE-SKY APPROACH TO UNDERSTANDING CLOUD FORMATION

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Recent developments in our basic understanding of ice nucleation are discussed that highlight the transformative potential of allying experiment, field measurement, and theory.

Clouds directly influence the planetary albedo and thermal radiation in opposite ways, and they hence largely determine the radiative energy budget of Earth, impacting the global temperature, weather, and society. However, understanding the factors that influence ice formation within clouds is a major unsolved and pressing problem and an important missing piece in our understanding of past, present-day, and future climate that is highlighted in the 2013 Intergovernmental Panel on Climate Change report (Boucher et al. 2013). Here, we outline recent breakthroughs that have significantly advanced our understanding of the field. These developments lead us to suggest that now there is an opportunity to make substantial progress toward understanding ice formation in the atmosphere. We argue that a concentrated effort should be dedicated to studying mimic/proxy materials, utilizing an array of investigative tools that span from the nanometer scale to cloud chamber experiments and atmospheric observations.

Crystallization of water is such a familiar process that one might presume that by the twenty-first century, the basic mechanism by which water freezes or "nucleates" into ice is well understood. However, water continues to reveal unexpected properties, such as that ice nucleates at different rates on oppositely charged plates of a pyroelectric (Ehre et al. 2010), a phenomenon that may be relevant to triboelectric charging (electrification of ice particles due to friction upon collision) in clouds and is yet not understood. Residues obtained from cloud ice crystals are dominated by mineral dust and biological particles (Pratt et al. 2009; Cziczo et al. 2013; DeMott 2003; Twohy and Poellot 2005), suggesting these species are important for ice formation. A key question in cloud formation then is what makes good ice nuclei? Although it has been known for decades that dust of

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various origins, bacteria, fungal spores (O'Sullivan et al. 2015; Hoose and Möhler 2012), and other biological particles, such as cellulose (Hiranuma et al. 2015) and diatom-infused sea spray (Wilson et al. 2015), can raise the nucleation temperature, a molecular-scale picture of why materials of disparate chemical composition and structural order can have similar ice nucleation efficiency is lacking. Recently, there seems to have been a breakthrough by Atkinson et al. (2013) who reported that K-feldspar (where K$^+$ is a countercation to the negatively charged alumino-silicate framework), a component in Saharan Desert dust, is an exceptionally potent ice nucleator (IN), inducing crystallization in otherwise pure water at around −15°C, more than 20°C above the temperature of spontaneous crystallization of pure water. Figure 1 shows the results of a dust-modeling study parameterized on desert dust sample data that shows feldspar

concentration and ice nuclei distribution centered on the Saharan region; feldspar is predicted to be a major contributor to observed IN densities.

The reasons for the exceptional potency of K-feldspar, metallic particles (Cziczo et al. 2013), and other very efficient ice nuclei, such as commercially marketed silver iodide and bacteria, to control cloud, ice, and snow formation are not clear. The classic text-book treatment of this topic (Pruppacher and Klett 1997) identifies five ingredients for an efficient IN: 1) insolubility, 2) size (potent ice nuclei are observed to be larger than the critical nucleus diameter of ice; this diameter depends on temperature), 3) chemical bonds (surface-accessible hydrogen bond acceptor/donor groups), 4) crystallographic match (the IN surface should have a close geometric match with one of the principal crystal growth planes of ice), and 5) active sites (experimentally it is observed that only
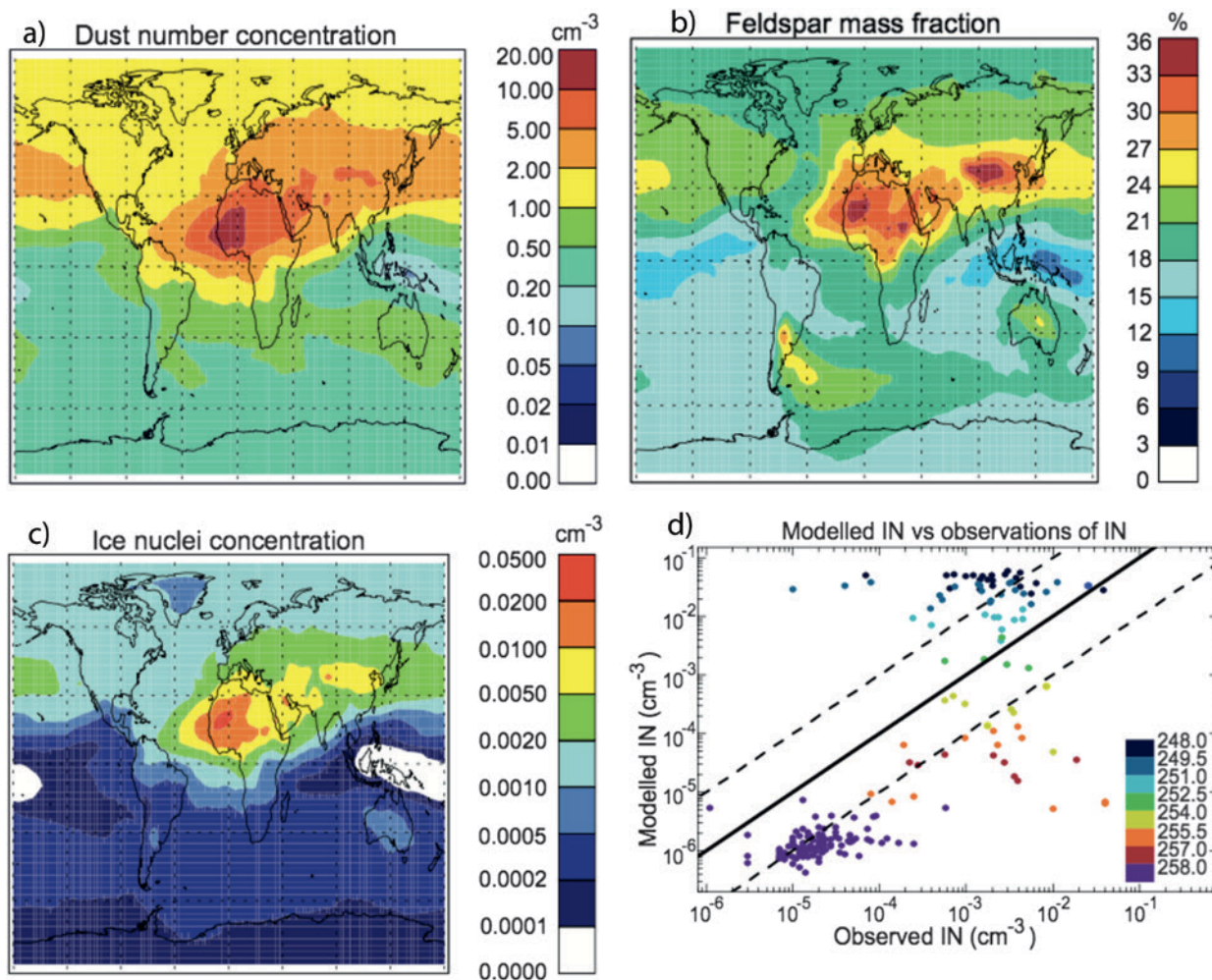


FIG. 1. The remarkable correlation between (a) dust particulate density, (b) feldspar density, and (c) ice nuclei density, concentrated over the Saharan region. (d) The good correlation between modeled and observed ice nuclei density over a 10-K temperature range. [Taken from Atkinson et al. (2013).]

a fraction of available surface area initiates crystallization; see also Fig. 2, taken from Thürmer and Nie (2013). Discriminating, for example, the role of bonding from crystallographic match and determining the structure of active nucleation sites and then assessing their importance in different atmospheric conditions requires a systematic, multipronged, and concerted approach. Although materials such as feldspars are very potent ice nuclei, their structures are a challenge to characterization and atomistic modeling approaches because of their complex chemical composition and low structural symmetry. A model material is clearly needed that is amenable to study by nanoscale modeling, microscopic and spectroscopic methods, and cloud chamber experiments, has IN potency, and hence is relevant to atmospheric observations. Quartz ($SiO_2$), for example, satisfies these criteria; it is a major component of desert dust [e.g., 16% (Atkinson et al. 2013)], it is a potent IN (e.g., Atkinson et al. 2013), and its structural chemistry is more tightly constrained than feldspar and clay minerals.

Although there is mounting data on the efficacy of different types of ice nuclei, one of the biggest gaps in our knowledge today is the scarce atomic-scale characterization data of IN active materials. In the case of IN minerals, what is the shape (as well as size) of the IN crystal? What faces are expressed? Does the aspect ratio (relative size of different crystal faces) of an IN affect potency? Are point defects (e.g., ion vacancies) and line defects (e.g., growth spirals) key "active sites" that trigger crystallization of ice? To begin to answer these questions, we need an array of spectroscopic techniques, including high-resolution confocal laser microscopy to identify surface topography (e.g., Sazaki et al. 2010), allied with atomic force microscopy and scanning tunneling microscopy (Fig. 2) to identify and establish how IN potency correlates to structural features. The latter techniques can be used to examine atmospheric and test dust samples, but other techniques can probe in situ interfacial structure directly. A recent study (Lis et al. 2014) beautifully illustrates how sum-frequency generation experiments can discern distinct structural layers at a $SiO_2$–water interface, showing that the bulk liquid flow rate of the water across the surface affects the water structure at the interface. Catalano (2011) has used small-angle x-ray scattering techniques to observe the layering of water at the corundum–water interface, which has recently been confirmed through novel atomic force microscopy and computer simulation studies (Argyris et al. 2013). Interestingly, the layering of water at interfaces has been phenomenologically linked to facilitating the nucleation of ice on sootlike
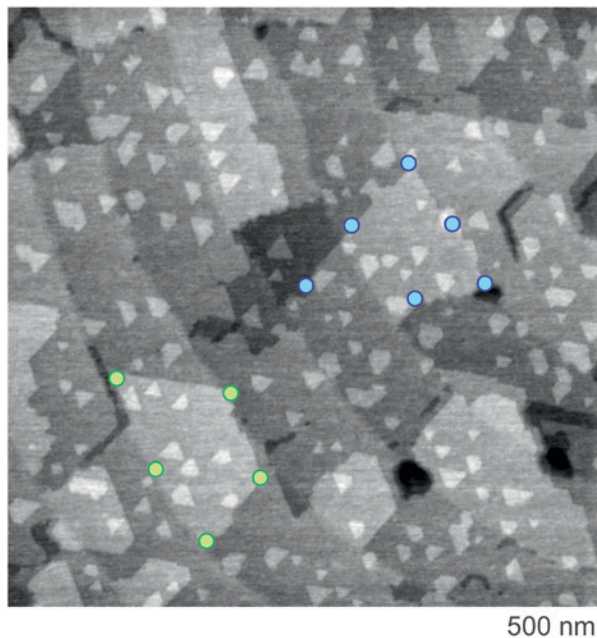


Fig. 2. Scanning tunneling microscopy image taken from Thürmer and Nie (2013) showing nascent triangular ice crystallites on an ice-monolayer-covered platinum surface. Triangular islands shown in blue and green have opposing orientation and when these individual crystallites coalesce, the formation of cubic ice can occur, facilitated by growth spirals.

and graphene nanoflakes (Lupi et al. 2014) and kaolinite (Cox et al. 2013) films according to nanoscale molecular dynamics simulations but the mechanism [and its generality (Cox et al. 2015a,b)] has yet to be extricated. Experimental in situ probes provide a way of examining how highly oriented deposited or grown substrates affect water at the interface, which can be compared and contrasted with experiments on distinct crystallographic faces of natural dust samples. Similarly, the nucleation efficiency of materials with identical nominal stoichiometry but different aspect ratio and step density can be compared in cloud chamber experiments (e.g., Hiranuma et al. 2014). Surface characterization methods and in situ spectroscopies provide a valuable feedback mechanism to nanoscale modeling. Atomistic modeling can be used to construct structural features on materials to assess whether, for example, growth spirals or steps accelerate or inhibit ice crystallization and the prediction cross referenced with in situ measurements and cloud chamber experiments.

The predictive capability of nanoscale modeling approaches has grown rapidly in the last few years and there have been a number of notable discoveries relevant to understanding the nucleation mechanism

in ice. Moore and Molinero (2011b), Li et al. (2011), and Sanz et al. (2013) have reported on detailed studies of homogenous ice nucleation, yielding estimates of the size of the critical nucleus as a function of temperature that compare well with those obtained experimentally. Moore and Molinero also showed evidence that as the homogenous nucleation temperature of approximately −41°C is approached, a rapid increase in the tetrahedrality and four-coordinated water molecules is observed and that extended patches of structured water are crucial for stabilizing critical nuclei. A vivid example of the predictive capability of simulation approaches can be seen in the work on the detailed structure of ice embryos, where supercooled water was shown to contain crystallized ice with sequences of hexagonal and cubic ice (Moore and Molinero 2011a). Consistent with those observations, a concerted study involving crystallization experiments, x-ray diffraction analysis, and direct computer simulation of crystallization showed that what has historically been referred to as cubic ice is in fact a stacking disordered ice structure $I_{sd}$ consisting of sequences of cubic and hexagonal stacking (Fig. 3; Malkin et al. 2012; Kuhs et al. 2012). Because $I_{sd}$ is metastable with respect to hexagonal ice, its vapor pressure is higher and hence its activity in cloud microphysics is distinct from hexagonal ice.
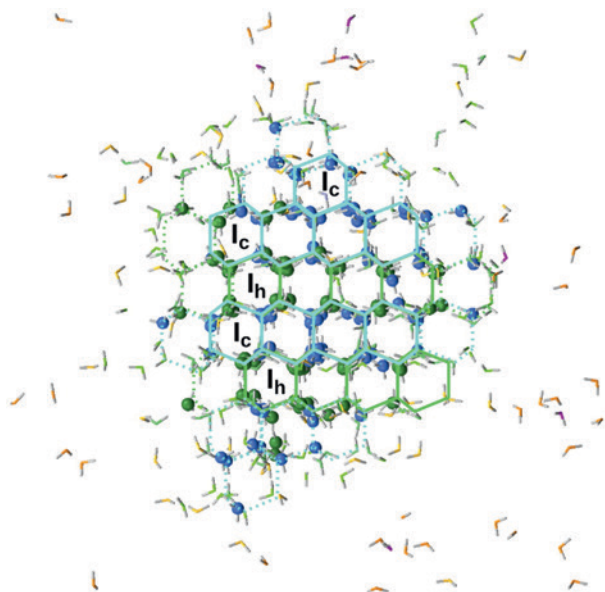
There have been transformative breakthroughs in recent years in understanding the structure of supercooled water (Sellberg et al. 2014; Moore and

Molinero 2011b) and the mechanism of crystallization of ice (Malkin et al. 2012; Moore and Molinero 2011a); developments in microscopy to follow in situ ice crystallization on model dust materials (Thürmer and Nie 2013; Sazaki et al. 2010); instruments capable of measuring all modes of the ice nucleation cycle, including techniques for measuring tropospheric water vapor concentration (Neely and Thayer 2011); methods of characterizing the structure of ice in clouds (Carr et al. 2014); the composition of cirrus clouds (Cziczo et al. 2013); the elucidation of aviation-induced contrail and cirrus formation (Burkhardt and Kärcher 2011); models that probe cloud microphysics, including supersaturation variability and its influence on ice nucleation (Kärcher et al. 2014); and the revelation of minor components in aerosol particles, which have a major influence on ice nucleation (Atkinson et al. 2013; Cziczo et al. 2009). With these developments in experimental techniques, modeling approaches, and the capability to simulate cloud microphysical processes in cloud chamber facilities such as the Aerosol Interaction and Dynamics in the Atmosphere facility (www.imk-aaf.kit.edu/73.php), there is an unprecedented opportunity to tackle the long-standing problem of ice nucleation in clouds. We suggest that a coherent study on an agreed set of materials would help to accelerate the rate of discovery in this area and bridge the gap between the atmospheric science community and materials science approaches. Model dust materials, such as quartz, are accessible to atomistic modeling approaches, state-of-the-art surface science, and characterization techniques, as well as crystallization and cloud chamber experiments. We believe that a combination of approaches is necessary to untangle cloud microphysical processes from the details of IN microstructure and their relative importance on ice and cloud formation and, ultimately, climate.

**FIG. 3. A nucleus of stacking disordered ice at −53°C, revealing an irregular sequence of hexagonal (green) and cubic (cyan) stacking. A pure cubic form of ice has never been experimentally isolated (Malkin et al. 2012).**

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