



# Pore condensation and freezing is responsible for ice formation below water saturation for porous particles

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Ice nucleation in the atmosphere influences cloud properties, altering precipitation and the radiative balance, ultimately regulating Earth's climate. An accepted ice nucleation pathway, known as deposition nucleation, assumes a direct transition of water from the vapor to the ice phase, without an intermediate liquid phase. However, studies have shown that nucleation occurs through a liquid phase in porous particles with narrow cracks or surface imperfections where the condensation of liquid below water saturation can occur, questioning the validity of deposition nucleation. We show that deposition nucleation cannot explain the strongly enhanced ice nucleation efficiency of porous compared with nonporous particles at temperatures below  $-40\text{ }^{\circ}\text{C}$  and the absence of ice nucleation below water saturation at  $-35\text{ }^{\circ}\text{C}$ . Using classical nucleation theory (CNT) and molecular dynamics simulations (MDS), we show that a network of closely spaced pores is necessary to overcome the barrier for macroscopic ice-crystal growth from narrow cylindrical pores. In the absence of pores, CNT predicts that the nucleation barrier is insurmountable, consistent with the absence of ice formation in MDS. Our results confirm that pore condensation and freezing (PCF), i.e., a mechanism of ice formation that proceeds via liquid water condensation in pores, is a dominant pathway for atmospheric ice nucleation below water saturation. We conclude that the ice nucleation activity of particles in the cirrus regime is determined by the porosity and wettability of pores. PCF represents a mechanism by which porous particles like dust could impact cloud radiative forcing and, thus, the climate via ice cloud formation.

ice nucleation | clouds | cirrus | deposition nucleation | pore condensation and freezing

Small volumes ( $\sim 10^{-11}\text{ cm}^3$ ) of pure water freeze at the homogeneous nucleation temperature (HNT, Fig. 1) of about  $-38\text{ }^{\circ}\text{C}$  (e.g., ref. 1). Heterogeneous ice nucleation must be invoked to explain ice formation at higher temperatures. In heterogeneous nucleation, an interface provided by an ice nucleating particle reduces the nucleation barrier, allowing the phase transition from liquid, or vapor, to ice (2). Cirrus clouds, composed entirely of ice, play a pertinent role in regulating the amount of long-wave radiation being emitted to space, necessitating a detailed understanding of the mechanisms responsible for cirrus cloud formation (3, 4). In situ studies investigating upper-level cirrus clouds over North and Central America and the Pacific found that heterogeneous nucleation dominates over homogeneous nucleation, and the observed ice formation was mainly attributed to deposition nucleation (Fig. 1) on mineral dust particles (5). Based on such observations, laboratory-based parameterizations of deposition nucleation have been incorporated in global climate models to predict ice-crystal number concentrations (6, 7), which influence Earth's radiative balance and ultimately future climate projections. However, laboratory experiments exposing atmospherically relevant dust particles to conditions below water saturation show a steep increase in the frozen particle fractions (i.e., activated fraction, AF) when the temperature falls below the

HNT (8, 9), suggesting that the liquid phase is involved in the nucleation of ice (9). This dependence led to the hypothesis that ice formation attributed to deposition nucleation is actually pore condensation and freezing (PCF) (10) (Fig. 1). PCF is defined as the condensation of liquid water in pores, cracks, steps, or capillaries (hereafter referred to as "pores") in humid air below water saturation by the inverse Kelvin effect (See *SI Appendix, section 2.1*), followed by homogeneous or heterogeneous freezing. Additionally, classical nucleation theory (CNT) predicts that ice embryos need to reach a critical size for macroscopic growth to occur. Thus, PCF is limited to the range of pore sizes large enough to accommodate a critical ice embryo, and narrow enough for condensation of liquid water to occur. Once pore ice is present, it has been proposed that ice can grow out of the pore as long as the ice-filled pore is large enough to accommodate the base of the critical embryo to nucleate ice from the vapor phase (11). The size of the pore required to sustain a nucleus that can grow directly from the vapor at atmospherically relevant conditions, however, is too large to permit condensation of water in the pore below water saturation (*SI Appendix, sections 2.1 and 2.2*), theoretically limiting the relevance of PCF. However, experiments investigating preactivation, or the ability of materials to nucleate ice more efficiently after being precooled below the HNT, found a dependence on the materials' porosity and pore-size distribution (12, 13). This suggests that ice

## Significance

The formation of ice at relative humidity below 100% is assumed to proceed without the presence of liquid water. However, it has been shown that liquid water can exist well below water saturation in narrow cracks and pores. Here we show that the barrier for deposition nucleation of ice directly from the vapor is insurmountable in experiments; liquid water is involved in ice formation on porous particles, regardless of the ambient humidity. Thus, our results render deposition nucleation unlikely for the formation of ice clouds in the atmosphere.

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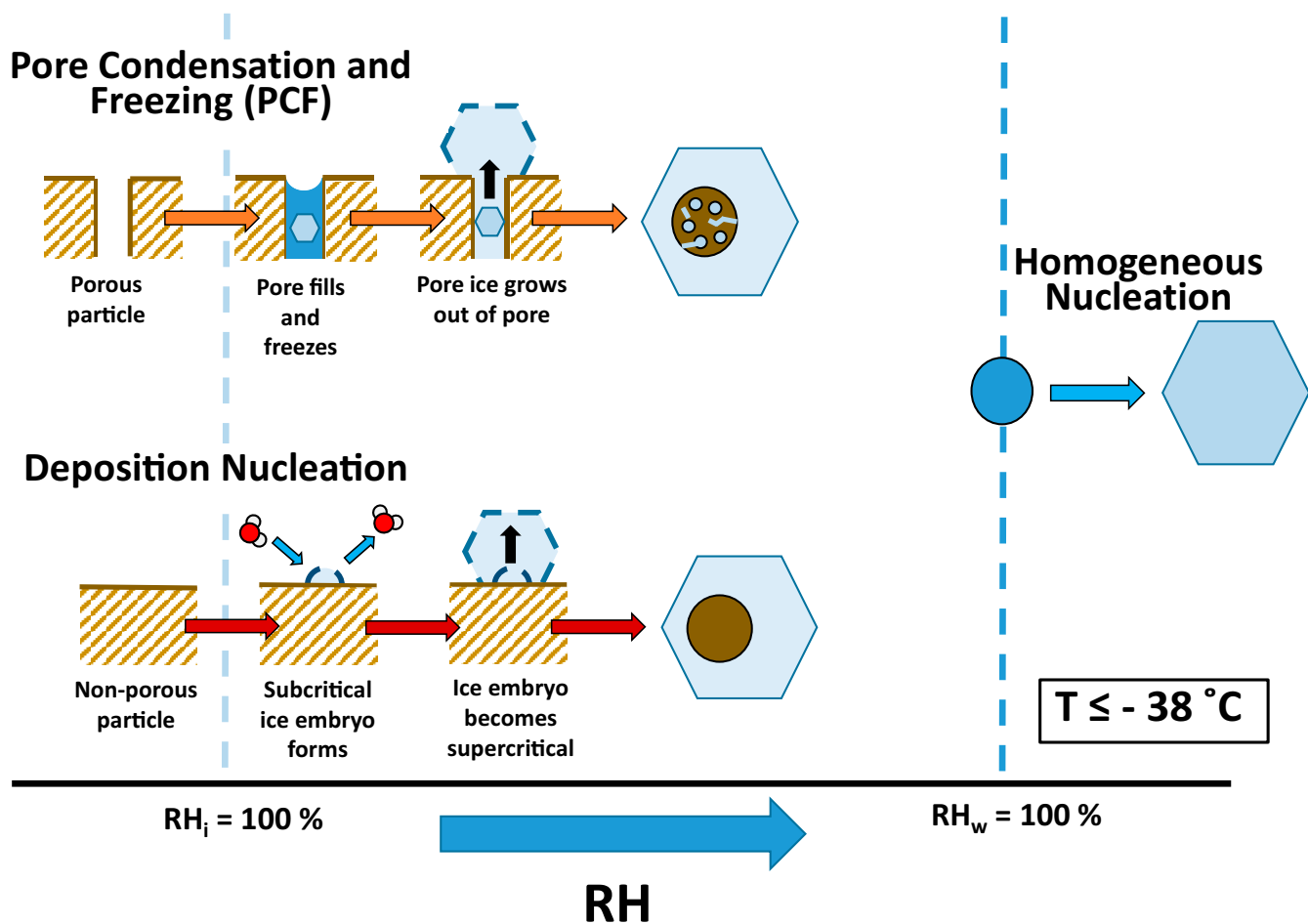


Fig. 1. Scheme of the pathways for pore condensation and freezing (*Upper Left*), deposition nucleation (*Lower Left*), and homogeneous nucleation of pure water droplets (*Right*), followed by ice-crystal growth. The vertical dashed lines indicate ice saturation (*Left*) and water saturation (*Right*).

can form homogeneously in pores and subsequently trigger ice growth out of the porous material at warmer temperatures. Furthermore, recent studies have shown that organic (14, 15) and water (16) vapors crystallize via the liquid phase condensed in wedge-shaped pockets, suggesting a PCF mechanism being responsible. Regardless, the generally accepted mechanism for ice nucleation below water saturation is currently deposition nucleation. Here we provide further evidence of the PCF mechanism by comparing the ice nucleation ability of synthesized porous and nonporous particles composed of the same material, in combination with CNT and molecular dynamics simulations.

## Results

Advances in material sciences have allowed for the synthesis of porous silica (significant component of atmospheric mineral dust) with well-defined pore diameters and morphologies (17). This allowed testing the so-called deposition nucleation with silica particles that have uniformly distributed 3.8-nm pores, as well as with nonporous silica particles (*Methods*). The ice nucleation ability of silica particles exposed to varying temperatures and ice supersaturations in the Zurich Ice Nucleation Chamber (ZINC) (18), shows a strong dependence on the presence of pores (Fig. 2). In Fig. 2A, the silica samples with monodispersed pore diameters of 3.8 nm (open symbols) show an increase in activated fraction at a much lower relative humidity with respect to water ( $RH_w$ ) than the nonporous samples (filled symbols) for  $-50 \text{ }^\circ\text{C}$ . Due to the inverse Kelvin effect, the 3.8-nm pores should be full at  $RH_w = 67\%$  (dashed line in Fig. 2A; see *SI Appendix, section 2.1*), which

corresponds to the  $RH_w$  at which the porous samples start to nucleate ice. It is important to note that this  $RH_w$  is also close to the required RH for ice crystals to grow to a detectable size in ZINC (*SI Appendix, section 3.1*). The observation of ice crystals at this  $RH_w$ , in combination with the ability of pores of this size to nucleate ice homogeneously (10, 19, 20), is strong evidence that the enhanced freezing ability of the porous samples is due to pore filling and subsequent homogeneous freezing of the pore water at or near the predicted  $RH_w$  for pore filling.

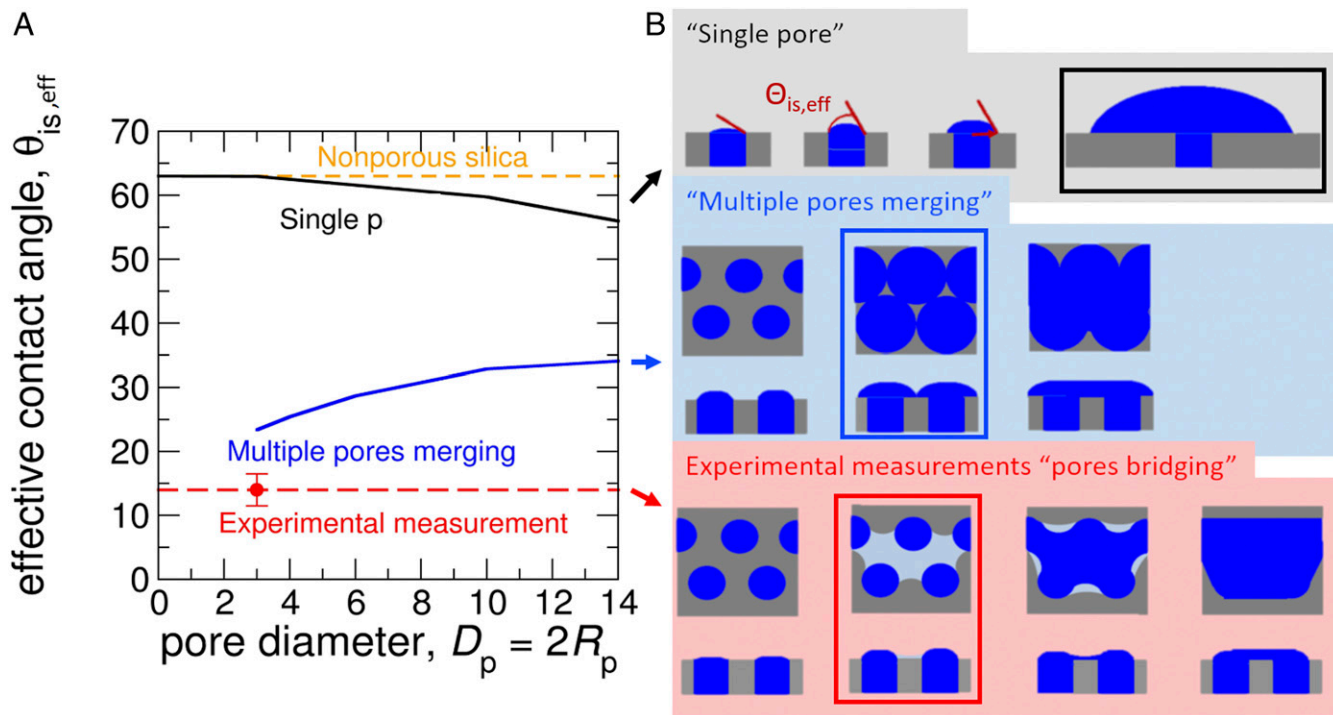
The ability of the nonporous silica particles to nucleate ice below water saturation (Fig. 2A) might suggest the concurrent presence of a deposition nucleation mechanism. However, applying CNT to the porous and nonporous particles we find that the barrier for deposition nucleation on nonporous silica is 8,000 times the thermal energy, rendering the barrier for deposition nucleation insurmountable on the timescales relevant to clouds or laboratory experiments (*SI Appendix, section 3.4*). Furthermore, high-resolution scanning electron and atomic force microscopy images (*SI Appendix, Fig. S1*) reveal the presence of imperfections and steps on the surface of the nonporous silica particles, which provide pore-like features for PCF to occur, albeit at higher  $RH_w$  than the truly porous samples. Therefore, the observed freezing on the nonporous particles suggests a PCF mechanism occurring due to the presence of surface imperfections.

At  $-40 \text{ }^\circ\text{C}$ , freezing for both porous and nonporous samples shifts to water saturation (Fig. 2B). The absence of ice nucleation activity of the porous sample is explained by considering the nucleation rate for homogeneous freezing of water inside the









**Fig. 4.** Effective contact angle between ice and the silica surface as a function of pore size for nonporous silica (yellow), a single pore (black), multiple pores merging (blue), and multiple pores bridging (red) is shown in A. The silica walls between the pores are taken to be 1 nm wide, irrespective of pore diameter. *SI Appendix, Fig. S8* presents the same kinetic information in terms of the ratio of the barriers for heterogeneous nucleation for each mechanism and the homogeneous nucleation pathway. (B) Sketches for ice growth for different scenarios. (Top) For a single pore, increase of contact angle at constant radius followed by increase of radius at constant contact angle, the black square marks the critical size. (Middle) For multiple pores merging scenario, the critical size is reached when the ice nuclei start to merge (indicated by blue square). (Bottom) For multiple pores bridging, condensation of liquid water between emerging ice nuclei is followed by crystallization of the liquid. Growth continues by freezing of condensed liquid water. Silica is pictured in gray, ice in blue, and liquid water in light blue.

**Particle Characterization.** Particle-size distributions were created by measuring at least 100 particle diameters with ImageJ on SEM (Quanta, FEG 250; see *SI Appendix, Fig. S1*) images. The nitrogen adsorption and desorption isotherms at  $-196^\circ\text{C}$  (77 K) were measured using a Quantachrome Nova 3000e system. The sample was pretreated at  $80^\circ\text{C}$  overnight in air and the pore-size distributions were obtained by nonlinear density-functional theory (NLDFT) calculations. NLDFT provides an accurate method to determine pore-size distributions (49) using theoretical isotherms to predict the pore-size distribution through a comparison with previous experimental data (50). As can be seen in *SI Appendix, Fig. S5*, a very narrow pore-size distribution is achieved with the synthesis method used in this study. The total surface area was obtained using the standard Brunauer–Emmett–Teller method for adsorption data in a relative pressure range from 0.05 to 0.30. The surface roughness of the nonporous particles was measured with atomic force microscopy (AFM; NT-MDT, SOLVER PRO). Before sampling in the AFM, dry nonporous particles were suspended in a hydrochloric acid suspension [pH = 2–3,  $\omega(\text{SiO}_2) = 1\%$ ] and then incubated on a glass slide overnight. The microscope was run in the noncontact mode and the particle curvature was fitted with a second-order polynomial to obtain a flat surface (*SI Appendix, Fig. S1*). Transmission electron microscopy [JEOL-JEM 1400 run with SlightX Viewer (JEOL)] was performed on the porous particles to ensure the spherical nature of the porous particles (*SI Appendix, Fig. S1*). The illite NX particles were not imaged in this study but have previously been examined in refs. 51 and 52.

**Ice Nucleation Experiments.** The particles used in this study were aerosolized using a rotating brush generator (Palas, RBG 1000) and then passed through a cyclone with a  $1\text{-}\mu\text{m}$  cut size (URG-2000–30EHB) before entering a  $2.7\text{-m}^3$  stainless-steel tank (53). The particles were then size selected to produce a quasi-monodisperse aerosol of 400 nm using a polonium source neutralizer and a differential mobility analyzer (Long DMA, model 3081; TSI Inc.) column before entering the continuous flow diffusion chamber, ZINC (18). However, due to multiple charging in the neutralizer, aggregates of particles larger than  $1\text{ }\mu\text{m}$  can pass through the DMA and enter ZINC where they are misidentified as ice (Fig. 2). The porous particles were observed to have a higher fraction of aggregates than the nonporous particles and this explains the difference in

the AF curves in Fig. 2 B and C before an increase in AF is observed. The size distribution of size-selected aerosols is presented in *SI Appendix, Fig. S5*. The secondary peaks at 200 and 300 nm are due to 400-nm particles being multiply charged. Further evidence that the peaks at these sizes are artifacts and not representative of the samples can be seen in *SI Appendix, Fig. S1D*, displaying an SEM image presenting the uniform size of the silica particles. In ZINC, the aerosol particles are layered between two-particle free-sheath flows of  $4.5\text{ L min}^{-1}$  each on either side of the  $1\text{ L min}^{-1}$  aerosol layer for a total flow rate of  $10\text{ L min}^{-1}$  (ref. 18). With a flow rate of  $10\text{ L min}^{-1}$ , the residence time in ZINC is  $\sim 10\text{ s}$  but varies with increasing ice supersaturation and temperature due to buoyancy effects in the chamber (18). To determine the ice nucleating ability of the samples tested in this study, particles were exposed to increasing RH, at a rate of 2% per minute for a selected temperature. The RH, where ice begins to form is determined by distinguishing larger ice crystals ( $1\text{ }\mu\text{m}$ ) from the smaller (400 nm) unactivated particles by an optical particle counter (OPC, Lighthouse, Remote 5104) at the bottom of the chamber. The activated fraction of the aerosol was calculated as the ratio of ice crystals (i.e., particles larger than  $1\text{ }\mu\text{m}$ ) detected by the OPC at the bottom of the chamber to the total number of aerosols entering the chamber determined by a water-based condensation particle counter (model 3787, TSI Inc.).

**Molecular Simulations of Ice Growth out of Nanopores Under Controlled Supersaturation.** To study the growth of ice on nonporous amorphous silica and porous silica we run molecular dynamics simulations in the grand canonical ( $\mu VT$ ) ensemble (GCMD) (54), coded into the MDS software LAMMPS (55). The dimensions of the periodic simulation cells are  $8\text{ nm} \times 8\text{ nm} \times 10\text{ nm}$ , containing a 5-nm-wide silica-like slab with either (i) no pores, (ii) a single pore of 3-nm diameter, or (iii) a triangular array of 3-nm-diameter pores separated by 1-nm silica walls. The latter corresponds to the arrangement of pores in the porous silica used in this work (32–34). The pores in (ii) and (iii) are filled with hexagonal ice exposing the primary prismatic face to vapor. Water is represented with the mW model (26). We consider two sets of parameters from ref. (54) for the interaction between the silica-like (s) walls and water (w): (i) a more hydrophilic silica (contact angle with water  $\theta = 0^\circ$ ), with a characteristic interaction energy of  $\epsilon_{ws} = 6.19\text{ kcal mol}^{-1}$ , a characteristic interaction size is



$\sigma_{ws} = 0.2392$  nm, and a measure of the tetrahedrality of the potential of  $\lambda = 23.15$  which at 25 °C reproduces (54) the experimental pressure of capillary condensation of pores in silica (56), and (ii) a less hydrophilic surface (contact angle with water  $\theta = 64^\circ$ ), which at 25 °C has a pressure of capillary condensation that is 6.7 times higher than in the experiment, is modeled with  $\epsilon_{ws} = 0.45$  kcal mol<sup>-1</sup>,  $\sigma_{ws} = 0.356$  nm, and  $\lambda = 0$  (54). We consider the first set to be more representative of actual silica.

We evolve the GCMD simulations at controlled supersaturation with respect to ice  $S_i = 2.5$  and 3.0 with respect to the vapor pressure of a slab of ice at  $-81$  °C, the temperature of maximum crystallization rate for mW water in the 3-nm-wide pore (20). Previous studies have shown that the mW water model reproduces the experimental supersaturations at a given temperature (54, 57).

The equations of motion are integrated with the Velocity Verlet algorithm with a time step of 5 fs. Temperature is controlled by Nosé–Hoover thermostat with a relaxation time constant of 0.5 ps. A number of attempts to insert or delete molecules are realized every time step to control the chemical potential

of the system, and this relation is called GCMD ratio. In this work we use a ratio of 20, which has been shown to give accurate supersaturations for mW water (54). We run the GCMD simulations at each  $S_i$  for about 200 ns. Ice is identified with the CHILL+ algorithm (58).

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